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INORGANIC

CHEMICAL PREPARATIONS

BY

FRANK HALL THORP, PH.D.

INSTRUCTOR IN INDUSTRIAL CHEMISTRY IN THE MASSACHUSETTS
INSTITUTE OF TECHNOLOGY

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PREFACE.

THIS little book owes its existence to the need, which the writer has experienced, of more specific instructions than can conveniently be given orally to students beginning a course of laboratory practice in inorganic preparation work. It is hoped that it will be of especial assistance to the instructor of large classes, by relieving him to a great extent from the wearying repetition of directions to individual students.

The preparations selected are the salts most used in the laboratory, or those of commercial importance. A few metallic salts of organic acids are included, because they are used in laboratory work, or are particularly fine examples of crystallization.

The raw materials required are, with few exceptions, inexpensive, and may be obtained in almost any locality, or prepared by methods given in this book. The utility and importance of by-products and laboratory residues are shown by employing them whenever possible.

The reactions, specific gravity of solutions, molecular weights, etc., given with each experiment, together with the tables in the appendix, furnish the necessary data from which the student is expected to make all computations involved. The approximate amounts of material and reagents are given with

each experiment, but are intended to be used merely as a check on his calculations, since errors occurring through haste or carelessness may cause much trouble and waste of time. The author considers this practice in calculating one of the chief features of the book, and would recommend that all figuring be required in full in the note-book.

No attempt has been made to observe any particular grouping or sequence in the preparations, and each is to be regarded as an independent experiment.

In the preparation of the work much has been drawn from the works of Bender, Erdmann, Fresenius, and other authorities indicated in the references.

In conclusion, the writer wishes to express his sincere thanks to Prof. H. P. Talbot, of the Massachusetts Institute of Technology, for valuable criticism and assistance in the correction of proof. He also desires to acknowledge his great obligation to Mr. J. W. Smith, of the same institution, to whose extensive practical experience many of the processes and modifications of methods and apparatus given in this work are due, and by whose teachings he has largely benefited through association as student and instructor.

F. H. T.

Boston, Mass., October, 1896.

INORGANIC CHEMICAL PREPARATIONS.

ABBREVIATIONS USED IN THE REFERENCES.

Am. Chem. J. = The American Chemical Journal. 1879–96 +.

Ann. = Annalen der Chemie und Pharmacie, by Liebig and others. 1832–96+.

Ann. Chim. Phys. = Annales de Chimie et de Physique. Paris. 7 series, 1789–1896 +.

Arch. Pharm. = Archiv der Pharmacie. 1882–96 +.

Ber. = Berichte der deutschen chemischen Gesellschaft. Berlin, 1868–96 +.

Bull. Soc. chim. = Bulletin des Séances de la Société chimique de Paris.

Chem. Centralb. = Chemische Centralblatt.

Compt. Rend. = Comptes-rendus hebdomadaires des Séances de l'Academie des Sciences. Paris, 1835–96 +.

Dingl. J. = Dingler's Polytechniches Journal. 1820–96 +.

Jahresb. = Jahresbericht über die Fortschritte der Chemie, u. s. w.

J. Am. Chem. Soc. = Journal of the American Chemical Society. New York, 1876–96 +.

J. pr. Chem. = Journal für praktische Chemie. Leipzig. 2 series, 1834–96 +.

J. Soc. Chem. Ind. = Journal of the Society of Chemical Industry. London, 1882–96 +.

Pogg. = Annalen der Physik und Chemie. 5 series, 1824–77.

Sheik. Verhand. = Scheikundige Verhandelingen en Onderzoekingen. Rotterdam, 1857–64.

Zeit. anal. Chem. = Zeitschrift für analytische Chemie. Wiesbaden, 1862–96+.

Zeit. angew. Chem. = Zeitschrift für angewandte Chemie. Berlin, 1887–96+.

Zeit. anorg. Chem. = Zeitschrift für anorganische Chemie. 1892–96 +.

PART I.

INTRODUCTORY.

SOLUTION.

BY solution is meant the union of a solid, liquid, or gas with a liquid, called the solvent, to form a homogeneous liquid. The dissolving of a gas is generally known as absorption; when one liquid is dissolved in another, they are said to be mixed; while the term *solution* is usually applied to the dissolving of a solid. Solutions are of two kinds, *chemical* and *simple*. In a chemical solution a combination takes place between the solvent and the dissolved substance, so that each loses its identity, and a new compound results. In a simple solution there is no chemical union between the solvent and the dissolved body, and each may be recovered unchanged, by physical methods. In the following preparations nearly all the simple solutions are made with water as the solvent. In very rare instances alcohol, ether, or other liquid may be used.

Generally the first step in any preparation is to dissolve the raw material in some solvent, or to bring into solution the product obtained as the result of a chemical action between raw materials. The majority of reactions are carried out with substances in solution. When the problem of bringing a certain substance into solution in water is presented, the first point to be decided is, *how much water is necessary to dissolve the given weight of the substance.* No large excess of water should be used, as it must be filtered or evaporated later, or it may dilute the solution beyond the point at which a desired reaction can

best be carried out. In general, solutions should be kept as concentrated as possible, and still permit of filtration or other manipulation, without the salt crystallizing during the process. As a rule (there are some important exceptions), the solubility of a salt increases as the temperature rises, until the saturation point is reached at the boil. A solution is said to be saturated at any given temperature when it will take into solution no more of the salt *at that temperature.* Only by increasing the heat can more salt be dissolved. A solution saturated at the boiling temperature cannot be filtered successfully on a bag or cloth filter, nor in an ordinary funnel, because exposure to the air, together with the cooling effect of the funnel walls or filtering material, will lower the temperature sufficiently to cause crystallization and consequent clogging of the filter. Only by intricate special appliances for maintaining the temperature of the funnel walls at or slightly above the boiling point can such solutions be filtered (p. 13). In laboratory practice it is best to work with solutions which would be saturated at temperatures 10° or 15° *below* that actually employed. This allows for considerable cooling of the solution before crystallization begins.

When a certain substance is to be dissolved, the student must ascertain its solubility,* decide at what temperature it is best to work, and then calculate how much water is necessary to dissolve the given weight of the salt at from 10° to 15° below this temperature.

As a rule the temperature employed should be as near boiling as convenient, except in the case of a few salts whose maxi-

* In the "Dictionary of Solubilities of Chemical Substances," by Frank H. Storer, or the new "Dictionary of Chemical Solubilities," by Arthur M. Comey, will generally be found the amount of a given salt which is held in solution at 0°, 15°, 50°, and 100° C.; and at the boiling point of the saturated solution. In connection with most of the preparations in this MANUAL the solubility at various temperatures and the specific gravity of the solution with varying per cent of the salt in question are given.

mum solubility lies considerably below boiling. But even in these cases, heating above the point of maximum saturation is no particular objection, since the capacity of the solution to take up more substance *increases* as the temperature falls to this point, and such operations as filtering may be performed without danger of the salt crystallizing on the filter.

Whenever a *crystallized* salt is to be dissolved, the student should take into account the "water of crystallization," if there be any in the crystal. In many cases this water may amount to even more than one-half of the total weight of the crystallized salt, and it should be deducted from the quantity calculated for the solution of the *anhydrous* salt. Likewise, when neutralizing or acidifying a solution, the water added in the neutralizing solution or in the acid must be taken into consideration, if in significant quantities. When working on a manufacturing scale the moisture mechanically enclosed in certain damp raw materials must frequently be regarded. This may sometimes amount to 10% or more of the weight of salt.

In most cases much time is saved by dissolving substances in hot liquids, and frequent stirring during solution is advisable. It is generally best to stir the solvent actively while introducing the material to be dissolved. This prevents, to a great extent, the tendency which some salts (*e.g.* soda ash) have to cake together in a solid lump, whose solution then becomes exceedingly slow. The finer the crystals or particles of a substance, the more rapid is its solution; hence coarse crystals or large lumps should be broken up in a mortar before attempting to dissolve them. Occasionally it is convenient to dissolve a substance by blowing free steam directly into the vessel containing it. In this way a strong solution can easily be made, and if the weight of dish and substance be known, the quantity of water thus added can be found by weighing the dish and the solution.

When a chemical solution is to be effected, the amount of the solvent needed should always be calculated from the chemical equation, due allowance being made for water or other inert matter contained in the solvent, or in the substance to be dissolved. The strength of the common acids used in these preparations should be determined from their sp. gr. (see DENSITY, p. 28) and from the tables given in the appendix.

When dissolving substances in acids where gaseous products are liberated and effervescence occurs, care should be taken not to fill the dish more than two-thirds full, and to add the substance to be dissolved in *small portions*, stirring thoroughly. Otherwise, loss of the solution from frothing over the sides of the dish is almost certain to occur.

It is also necessary to dilute concentrated acids before attempting to dissolve dry substances in them, except in a very few special cases. If this is not done, the student will be troubled with a large mass of "insoluble residue," due to the fact that there is not sufficient water present in the liquid to dissolve the salt formed in the reaction. Moreover, the decomposition of the substance is very incomplete in such cases, as its particles become coated with a layer of the salt, which prevents further action by the acid. Students frequently add more acid in this case, under the mistaken idea that that which is present has become neutralized; but a little water is often sufficient to set up vigorous action and afford complete solution.

It is generally best to add the *solid to the* solvent, but if it be found more convenient to add the solvent to the solid, the latter should first be made into a paste with a little water, and the solvent introduced in small quantities at a time.

In no case should large amounts of any solvent other than water be poured upon a dry substance at one time or without stirring.

PRECIPITATION.

One of the most frequently employed operations in chemical preparations is precipitation, by which a solid is thrown out from solution by the addition of a suitable reagent, called the precipitant. The precipitate is insoluble, or nearly insoluble, in the liquid from which it is separated. Precipitation may be done in hot or cold solution, but is generally more complete when the former is employed. When adding a reagent for the purpose of precipitating some constituent from solution, active stirring is always essential in order that the precipitation may be complete. The precipitating reagent should be added slowly and in small quantities at a time, and the mixture well stirred after each addition before the next is made.

Care must be taken in most instances *not to add an excess of the precipitant.* The exact point at which the precipitation is complete is often difficult to determine, and hence careful calculation of the amount of precipitant necessary for the case in hand should always be made from the equation, before beginning the experiment. It often happens that the solution changes from acid to alkaline, or *vice versa*, or becomes neutral, when the precipitation is completed. Thus, tests with litmus or other indicators furnish a means of control in the process. But in many instances it is necessary at frequent intervals to filter off a few drops of the liquid into a test tube, and then add a single drop of the precipitating reagent to this test. The formation of more precipitate in the test portion shows that the process is still incomplete, and more reagent must be added to the main mass of the solution. Toward the end of the precipitation the test will show only a faint cloud when the drop of reagent is put in. In the case of very heavy precipitates which settle quickly, it is often only necessary to wait for this subsi-

dence, and then add a few drops of the reagent to the supernatent liquid to determine whether precipitation is complete or not.

Precipitation should not be carried on in a very concentrated solution, as it is then difficult to obtain a complete reaction, owing to the bulk of the precipitate in the relatively small amount of liquid.

When the precipitation is accompanied by the evolution of gas, it becomes necessary to exercise much care, adding the reagent in small quantities, with active stirring. Otherwise the liquid may froth over the top of the dish, owing to the inclusion of bubbles of gas by the more or less pasty precipitate.

When all thrown out of solution, the precipitate is separated from the supernatant liquid by filtration or decantation and well washed by methods given under "Washing."

FILTRATION.

Filtration is the process of separating suspended solid matter from a liquid by causing the latter to pass through the pores of some substance, called a filter, leaving the solid matter on the filter. The liquid which has passed through the filter is called the filtrate. The filter material may be paper, cloth, unglazed earthenware, cotton wool, asbestos, slag or glass wool, sand, or other porous matter. In the following exercises paper, cloth, or asbestos will be frequently required.

There are numerous methods of filtering, and the selection of the one best suited to the work in hand is often a considerable problem.

Filtration by Gravity.

The ordinary method of filtering by use of paper supported by a funnel is too well known to need description here, but a few words concerning its use in special cases may well be included.

When very rapid filtration is necessary, *e.g.* when filtering a hot, nearly saturated solution, from which the salt crystallizes on cooling, plaited filters prepared according to well-known methods are advantageous. Other methods of rapid filtration will be mentioned below.

When using large filters and funnels holding considerable masses of liquid, the hydrostatic pressure on the point of the filter is often sufficient to burst the paper. This annoying accident may sometimes be prevented by using a small cone of very thin platinum foil, perforated with numerous fine holes, and fitting closely to the walls of the funnel. But a small filter made of the so-called "hardened" filter paper, and placed in the point of the funnel before fitting the large filter, serves nearly as well as the platinum cone. Another very convenient way of supporting the filter is to fold in with the paper a small piece of muslin or thin cotton or linen cloth. (See Fig. I.) Thus, in using an 8 or 10-inch funnel a piece of cloth 4 inches square may be folded in with the paper so as to extend about 2 inches from the point up the sides of the filter. First fold the circular piece of filter paper in halves ; then lay the piece of cloth smoothly on a table and bring the center of the paper

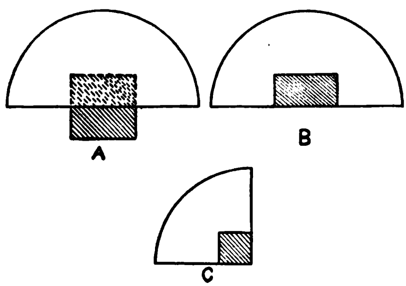


Fig. I.

as nearly as possible over the center of the cloth and lay it flat. (Fig. A.) Then lay the loose half of the cloth back over the paper (Fig. B), and fold both paper and cloth into quarters. (Fig. C.) When using plaited filters the cloth cannot be folded in with the paper so readily, but may be folded separately and placed in the point of the funnel before introducing the paper.

In many cases, especially in technical work, plain cloth filters are used. These may be pieces of cloth, folded to fit in funnels, or in the form of bags, supported on wooden frames. (In all cases the cloth should be well *boiled* in water, to free it from dirt, starch, clay, or other filling material, and to thoroughly wet the fibers before use.) These frames (see Fig. II) are made of pine about 16 or 18 inches square, and the legs are of sufficient length (about 16 inches) to allow a 4-gallon stoneware crock to be passed under. A few smaller frames will also be found convenient. The filtering cloth best suited to these frames is common unbleached sheeting, which should be torn in square pieces about 3 inches longer on the side than the width of the frame to be used. This allows for shrinking when the cloth is boiled, and yet leaves sufficient "bag," when placed on the frame, to hold a considerable amount of the liquid to be filtered. The cloth is fastened to the top of the frame by copper tacks, placed at intervals of from 2 to 4 inches, according to the character and weight of the liquid and residue. The cloth must not be stretched tightly over the top of the frame, but allowed to form a deep "bag." It is advantageous to keep the filter full

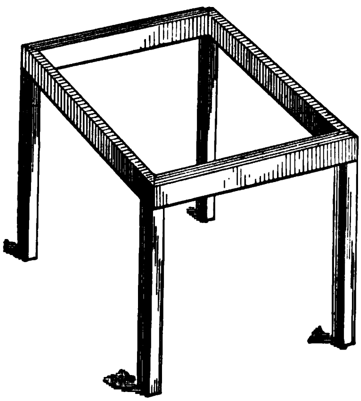


FIG. II.

of liquid while filtering, as the process is then more rapid and oxidation or other change less likely to occur. As a general rule, masses of liquid and precipitate amounting to less than two liters should be filtered in funnels. Larger quantities of liquor, containing very small amounts of sediment, may often be filtered in funnels also; but if the bulk of the *sediment* amounts to much over 1 to 1½ liters, the filter frame should be used.

Whenever *hot* solutions are to be filtered, it is necessary to fill the cloth filter with boiling water immediately before using, and allow this to run through for about a half minute. Then throw away what water remains in the filter, quickly place the stand over the receptacle intended for the filtrate, and pour in the solution to be filtered as rapidly as possible until the filter is full. If this proceeding is omitted, the cold filter cloth may chill the solution and cause crystals of the salt to form in the filter itself, which is thus rapidly clogged, and filtration becomes exceedingly slow. When such a mishap occurs, time is saved by transferring the liquid to a dish, and pouring boiling water into the filter, or, if possible, blowing free steam into it until these crystals are dissolved. Then the filtration must be started again, after heating both liquid and filter as above described.

Frequently when a turbid liquid is poured into a cloth filter, the filtrate will run through turbid at first. In such cases pour the liquid to be filtered, rapidly into the filter until this is full, and catch a few cc. of the filtrate in a casserole, at intervals of about a minute, until it is found that it runs clear. Then push a clean receiver under the stand and return the turbid filtrate to the filter. By the exercise of care and patience clear filtrates may be secured even in very obstinate cases. One of the most frequent causes of turbid filtration with cloth filters is the practice of students of scraping or rubbing the cloth with spatulas,

stirring rods, etc., with the idea of making the process more rapid. This proceeding will *invariably* result in turbid filtrates.

In many cases it is advantageous to use two cloths on the filter stand, — one fastened with tacks and the other laid loosely on it, to receive and hold the sediment. By this means the precipitate may readily be removed from the stand, washed by decantation (p. 20), and returned to the filter. In the case of slimy precipitates, frequent removals for washing become necessary.

In technical work, filter bags of felt or woolen cloth are sometimes used when greater thickness of filtering material is needed than is offered by linen or cotton cloth, or when the liquid is of a nature to destroy or corrode vegetable fiber. For liquids having destructive action on vegetable and animal matter, the use of asbestos, slag wool, or glass wool becomes

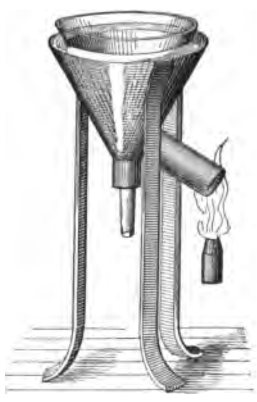


FIG. III.

FIG. IV.

necessary. Asbestos and slag wool should be treated with acid and well washed before using, to remove soluble lime, iron, or other salts which might contaminate the filtrate. Glass wool

is too expensive for general use, and in but few cases will its employment be necessary in the preparations in this book.

A plug of cotton wool, long-fiber asbestos, or glass wool loosely inserted in the neck of a funnel will often serve to remove sediment from a liquid rapidly and neatly.

Occasionally it is necessary to keep the temperature of the liquid in the funnel as high as possible during filtration. To do this an ordinary hot-water funnel is advantageous. This consists of a glass funnel, surrounded by a tin or copper jacket containing water, which is kept hot by the flame of a lamp under a projecting arm of the jacket. (See Fig. III.) Or the funnel is surrounded by a coil of copper, iron, or tin pipe, through which steam or hot water flows. (See Fig. IV.)

Filtration by Suction.

In order to gain time in filtering, it is often customary in laboratory work, and sometimes on a technical scale, to apply suction to the under side of the filter, thus forcing the liquid through by atmospheric pressure. In laboratory work on a small scale, the use of a glass or brass water-jet suction pump is very general. This will be assumed as the source of vacuum in the subsequent preparations. To make these pumps work successfully a good pressure on the water pipe is necessary. With *e.g.* forty pounds water pressure, the pump should give a vacuum of from 50 to 65 cm. of mercury when exhausting a vessel of two liters' capacity.

Funnels with paper filters, supported by cones of platinum or hardened paper, together with the ordinary filtering flask with side tube (see Fig. V), may be used with these pumps. But for most of the following preparations where suction is to be employed, one or the other of the methods given below will afford the best results.

The porcelain filter funnel, invented by Dr. Büchner (see Fig. V), is fitted to a common filtering flask by slipping a short piece of three-quarter-inch rubber tubing over the stem of the funnel, inserting it in the neck of the flask, and pressing it down so that the rubber makes an air-tight joint. Then a circular-cut filter of paper or cloth of *exactly the same diameter* as the perforated plate is carefully adjusted on this plate, taking care that there are no creases, and that the edges are all horizontal. The filter is then wet with distilled water, connection is made with the pump, and the suction turned on. *After*

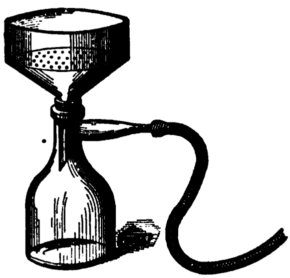


FIG. V.

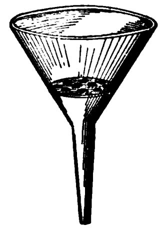


FIG. VI.

the suction is turned on fill the funnel to within a quarter of an inch of the top with the liquid to be filtered. If filled *before* the suction is turned on, the filter will be displaced by the liquid when it is poured in.

Should the first runnings be turbid, it is usually because the pores of the filter have not been sufficiently closed by the wetting to retain the finer particles of the sediment; but after a short time the pores will be closed by the solid matter and the filtrate will run clear. Now loosen the funnel from the filter flask to relieve the vacuum, and remove it entirely (letting the pump continue its suction), pour out the turbid filtrate, rinse the flask with a little water, and replace the funnel. If, however, the filtrate does not run clear after a few moments,

it is because the filter has not been properly fitted, — a crease has formed near the edge, or a hole has been made in the filter paper.

A modification of this method consists in using in an ordinary glass funnel the small perforated glass or porcelain plates invented by Dr. O. N. Witt. (See Fig. VI.) But these afford a small filtering surface, and are difficult to fit snugly against the funnel walls. They are very good, however, for supporting an asbestos or glass-wool filter.

The apparatus for the following method of filtration, devised by J. W. Smith, F. C. S., of the Massachusetts Institute of Technology, can be fitted up very simply and inexpensively. An ordinary 5 or 6 cm. glass funnel is covered with a piece of cloth drawn *tightly* across its mouth, the edges of the cloth being brought together and tied with a string closely around the stem at the base of the funnel. The stem of the funnel is then inserted in one end of a piece of rubber tubing about 50 cm. long. The other end of the tubing is connected with a bent glass tube which passes through a two-hole rubber stopper in the neck of an ordinary two-liter narrow-mouth bottle. By means of the second hole in the stopper, connection is made with the filter pump. A piece of filter paper is then laid on the cloth over the funnel mouth and moistened with water. The suction is then started and the paper drawn snugly against the cloth and edges of the funnel. The excess of paper outside the funnel's edge is then carefully torn away, leaving a smooth disc of paper entirely covering the mouth of the funnel and backed by the cloth. Holding the funnel by the stem, its mouth is carefully inserted in the liquid to be filtered, without disturbing any sediment which may have settled out. If the suction be very strong, the cloth over the mouth of the funnel and the paper covering it will cup a little, and it is necessary to insert the funnel into the liquid with

care, to avoid enclosing an air bubble, which would retard filtration very much. By introducing the funnel with its stem at an angle of 45° to the surface of the liquid, this difficulty may be avoided, and the filtration proceeds normally. This may be called an upward filtration, for the liquid is drawn off from above the sediment. The advantages of this method are: the pores of the filter are not so quickly clogged, large quantities of solution may be filtered rapidly, and the process may be instantly stopped at any time by removing the funnel.

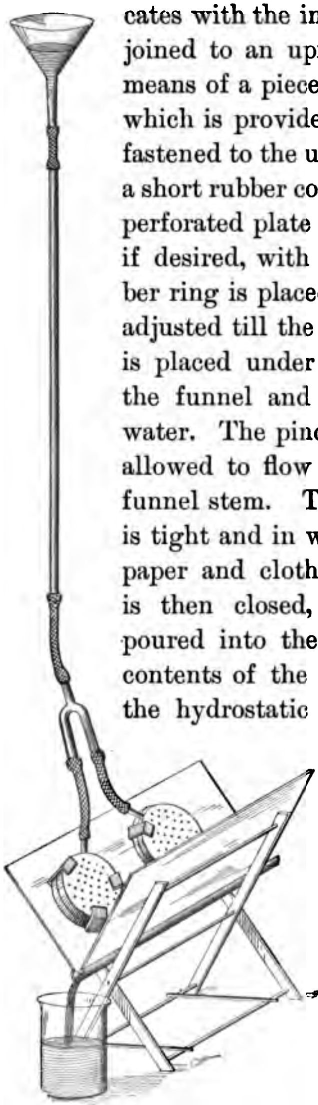
Unglazed earthenware balloons may be used in a similar manner to the small funnel above described, but without cloth or filter paper. The sediment collects on the outside of the balloon, while the liquid percolates through the interstices of the unglazed clay. These work very well, especially for very fine sediments, if a powerful suction be accessible, but are not so rapid nor easily managed as the apparatus already described.

Suction may be applied when filtering with asbestos, cotton or glass wool, if these substances are supported by perforated plates or cones.

Filtration by Pressure.

Filtration by means of the filter press is the mode generally employed in manufacturing operations, but these machines are not well adapted for use in such small work as laboratory experiments. There are small filter presses in the market, purporting to be for laboratory use, but the following much simpler form of pressure apparatus will generally be found more convenient, except when very high pressures are desired. (Fig. VII.)

This consists of two perforated porcelain plates about 15 cm. in diameter, separated by a rubber ring about 1 cm. thick, and fastened together by screw clamps. A short glass tube communi-



cates with the interior of the cell thus formed, and is joined to an upright glass tube about 2 m. high, by means of a piece of rubber tubing about 15 cm. long, which is provided with a pinch cock. A funnel is fastened to the upper end of this upright glass tube by a short rubber connection. The inner surface of each perforated plate is covered with a piece of cloth and, if desired, with a piece of filter paper also, the rubber ring is placed between the plates, and the clamps adjusted till the apparatus is tight. A tray or trough is placed under the cell to receive the filtrate, and the funnel and upright glass tube are filled with water. The pinch cock is then opened and the water allowed to flow until its level just sinks within the funnel stem. This will show whether the apparatus is tight and in working order, will moisten the filter paper and cloths, and expel all the air. The cock is then closed, and the liquid to be filtered is poured into the funnel. On opening the cock the contents of the funnel flow down into the cell, and the hydrostatic pressure forces the liquid through the filter, leaving the precipitate in the form of a cake in the cell.

As the last of the turbid liquid passes from the funnel into the vertical tube, water is poured into the funnel. This maintains the hydrostatic pressure and washes the cake of sediment. More water is added until the cake is washed sufficiently, when the apparatus is allowed to empty itself of the water, the cell is taken apart, and the cake removed.

Fig. VII.

Centrifugal Filtration.

For separating mother liquors from crystals, small centrifugal machines prove very convenient. (See Fig. VIII.) These may be had from 2 to 4 liters' capacity, and the smaller sizes are provided with two baskets — one of porcelain and one of tinned copper. If power be at hand, a larger machine, which has one large basket of tinned copper, will often prove useful. By lining the basket with cloth, even very fine crystals may rapidly be freed from the mother liquor, but the machine should never be used for fine non-crystalline precipitates.

Fig. VIII.

In all cases the machine should be taken apart and well washed *immediately* after use.

Pressing.

Granular or crystalline precipitates may be very conveniently freed from water by means of the knuckle-joint or screw press. Drain the precipitate in a strong cloth filter, fold the sides and ends of the cloth over the precipitate so that it cannot escape, and the pressure will be evenly distributed, and put into the press. By applying the pressure slowly and regularly the water may be driven out very thoroughly, leaving the precipitate in a solid cake. Pressing in this way is frequently recommended in the following preparations.

DECANTATION.

It often happens that a precipitate is of such a slimy nature that it soon chokes the pores of any filter, and filtration becomes exceedingly slow and tedious, even with powerful suction ; or the precipitate is of such a fine character that it passes through the filtering substance and turbid filtrates result.

To overcome these difficulties a process known as *decanting* is frequently employed, as follows. The liquid is allowed to stand quietly for some time (determined by the nature of the sediment) until the solid matter has all subsided, forming a layer on the bottom of the vessel. By carefully tipping the dish a large part of the clear top liquor may be poured off without disturbing the precipitate ; or the clear liquid may be drawn off by the use of a glass or rubber tube as a syphon. The small amount of liquid remaining may then be filtered from the precipitate by any one of the various forms of filter with but little trouble. When the main mass of the precipitate settles but leaves a few flocks of sediment floating on the surface or scattered through the liquid, the liquid may be drawn off very advantageously by upward filtration, as described on page 15.

FIG. IX.

Decantation is also very convenient in washing certain precipitates to free them from soluble matter. Large quantities of water may be used at each washing and quickly drawn off after settling (p. 20). This process may be greatly facilitated by the use of decanting or precipitation jars. (See Fig. IX.) These are porcelain or earthenware jars with tubulatures at various heights on the sides. The tubulatures are closed by corks or rubber stoppers, and the

liquid carrying the precipitate is poured in. The stoppers are removed from the orifices above the surface of the precipitate after it has subsided, and the top liquid is allowed to run off.

Decantation is also employed for very corrosive or caustic liquids which would attack the material of almost any filter.

WASHING.

The purpose of washing is to remove soluble matter mechanically enclosed among the particles of the precipitate. It is necessary, first, when the *precipitate* is to be used further, in which case this soluble matter would constitute an impurity in the product, and therefore must be removed, even though it has no value in itself; and second, when the *filtrate* contains the substance desired and the bulk of the precipitate is more than a very small fraction of the liquid filtered; for soluble matter, in itself valuable, may be retained in the precipitate and so lost.

The simplest method of washing is to pour water over the precipitate as it lies on the filter, allowing the water to percolate through, carrying the soluble matter with it. It is generally best to allow one portion of water to run through entirely before adding another. This method is best employed when the wash waters are to be evaporated to recover the soluble matter. In some cases the precipitate may be removed from the filter, stirred up with considerable excess of water, and poured back on the filter, this process being repeated as often as is necessary.

Washing by decantation is one of the most efficient methods of removing traces of soluble matter from dense or heavy precipitates which subside quickly, so that the process is very rapid. The precipitate is stirred up with a large excess of

water in a decanting jar (p. 19) and allowed to settle, and the clear water is drawn off, the process being repeated as often as need be.

When the filtrate contains a substance which is to be recovered, it is advisable to add the first two wash waters to the filtrate and evaporate all together. The subsequent wash waters are too dilute to be worth evaporating unless they contain very valuable salts, or are from large masses of precipitate, when it is customary to wash the sediment until the wash water reaches a gravity of from 1° to 2° Tw. (0.005 to 0.010 sp. gr.), and evaporate the combined wash waters.

If the precipitate is the product desired, washing is continued until a test of the wash water, as it comes from the filter, shows no trace of soluble impurity.

Crystals may be washed free from the mother liquor in the centrifugal machine by spraying a little water over them while the machine is in rapid motion, or by pouring a little water over them when they are in the draining cones. *Cold* water should always be used, and as little of it as possible, to avoid undue solution of the crystals.

In the case of *insoluble* precipitates and residues, it is generally best to use *hot* water for washing, whatever the method employed.

EVAPORATION.

In order to obtain the soluble salts contained in a dilute solution, the liquid is evaporated to such a concentration that the salts will crystallize from it. Evaporation is also practiced to decompose or drive off undesirable substances present in the solution, or to remove certain volatile liquids from others of higher boiling point.

It may be carried on in several ways: by direct heating over free flame, or by steam coils, or by a steam, water, or sand bath, or in a hot air closet; or by spontaneous evaporation in the open air, or in closed vessels (desiccators) over sulphuric acid, calcium chloride, caustic potash, or other water-absorbing substance.

Solutions which decompose on heating in the open air may be concentrated in desiccators, in which case the use of vacuum greatly accelerates the process, or at low temperatures (50° C. or less) in the warm closet. Active boiling over free flame or the use of a steam coil is the most rapid method of evaporation, but should not be used for very concentrated solutions, as loss may occur through spattering or by decomposition or volatilization of the salt. As soon as saturation is reached it is safer to transfer the dish to the steam or water bath if the evaporation is to be continued. In no case should a porcelain dish be placed over a lamp if there is a precipitate or mass of crystals on the bottom, unless the contents of the dish are stirred constantly and actively during the heating; otherwise the dish is almost certain to crack. Solutions may be evaporated to dryness on the steam or water bath, without risk of breaking even the largest dishes or of loss from spattering. Due care must be exercised in the evaporation of caustic alkali solutions in porcelain dishes lest the glaze be attacked if a certain concentration be exceeded. Dishes should be put where they will be free from dust during evaporation.

Distillation under diminished pressure is occasionally employed in preparation work, but very few of the subjects in this book require such treatment. When such is the case directions will be given in connection with the experiment.

CRYSTALLIZATION.

Crystals are chemically homogeneous bodies having regular polyhedral forms. The tendency to form crystals is common to almost all chemical compounds under certain conditions, and the forms of the crystals are characteristic of the substance. Crystals may form from solution, from a fusion of the substance, or by sublimation. In a vast majority of cases crystallization takes place from solution. During its formation there is a tendency to exclude from the crystal all matter not homogeneous with it. Hence, if the crystallization is not too rapid nor the solution too concentrated, this process is important as a means of purifying salts.

The liquor remaining after crystals of a salt have been deposited is called the "mother liquor." It contains much of the impurities present in the original solution and also considerable quantity of the salt which has not crystallized, the amount depending upon the concentration of the original solution and the temperature at which the crystallization took place. In the following preparations the concentration of the solution which affords the best crystals is stated in almost every case. In evaporating a solution to crystallize a certain salt from it, tests of its density should be made from time to time with a hydrometer (DENSITY, p. 28), until the proper concentration is reached; then, if large crystals are desired, the solution is allowed to cool slowly where it will not be disturbed. By rapid cooling, especially if the solution is stirred, very fine crystals called crystal meal are formed. These small crystals are often preferred in technical work because of their ready solubility.

If small crystals are desired and *the solution contains no impurities*, *i.e.* has been purified before evaporation, it is gen-

erally sufficient to evaporate it to saturation, which is shown by the formation of a skin or pellicle over the surface. This pellicle is due to minute crystals of the salt separating out of the solution and floating on its surface. But no *impure* solution should be treated in this way, because the crystallization is so rapid that particles of mother liquor and impurities become entangled among, and enclosed in, the crystals.

The volume of the solution has a marked effect on the size of the crystal, a small amount seldom yielding large crystals even under the most favorable circumstances. When large crystals are desired a considerable quantity of the solution, not too highly concentrated, must be set away where it will not be disturbed after evaporation and allowed to cool slowly. Or if a small crystal is put into a small quantity of solution, set under a bell jar together with a dish of sulphuric acid to absorb the moisture, and allowed to stand for some days at the temperature of the room, the crystal will sometimes "grow" by accretions of the salt until it reaches considerable size.

After evaporation, when the solution has reached the temperature of the room, and has remained at that temperature for *several hours*, the mother liquor is poured off from the crystals which are deposited on the sides and bottom of the vessel. The crystals are placed in a porcelain draining cone, or in a funnel having a perforated porcelain plate in its throat, and are allowed to stand until the adhering mother liquor drains away; or they are spread on porous plates of unglazed pottery or on filter or blotting paper which absorbs the moisture; but this is seldom practiced in technical work. Except when obtained from a *pure* solution, the crystals must be washed. (See WASHING, p. 21.)

By evaporating the mother liquor a second crop of crystals is obtained, which, however, are not so pure as the first; a third or fourth crop of still less purity may be secured in the

same way. Impure crystals are purified by redissolving in distilled water, and repeating the operation of crystallization.

When some solutions are allowed to crystallize the phenomenon of "creeping" is observed. This is especially true of ammonium salts and of some sodium and potash salts. Creeping is caused by the formation of minute crystals at the junction of the surface of the liquid with the sides of the dish. The narrow space between the dish and the crystals forms a species of capillary passage through which the solution rises, and, evaporating, deposits its contents of dissolved salt on the upper end of the crystals already formed, increasing their length and extending the capillary passage. If not interrupted this process may continue until the top of the dish is reached and the crystals extend over the edge of the dish and down the outside. Creeping may be prevented by smearing the edge of the dish with a *very thin* layer of paraffine oil or vaseline, applied with the finger; but care must be taken that this layer is very thin, or the contents of the dish may be contaminated. It is better to watch such salts carefully during crystallization, and by pushing such crystals as form above the surface back into the liquid, creeping may be controlled. While crystallizing, such salts should not be left more than 24 hours without examination.

DRYING.

Crystals or precipitates forming a finished product must be thoroughly dried before being put into bottles, the method employed depending upon the character of the product.

The laboratory should be fitted with a drying closet, preferably one having several compartments which can be kept at constant temperature by steam coils or by hot air. About four

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closets with temperatures ranging from 20° to 100° or 105° C. will be found convenient. A good circulation of air through the closet is to be desired. Water baths and water-jacketed drying ovens are often useful, but are rather too hot for drying soluble precipitates or crystals containing any "water of crystallization." Hot-air drying ovens heated by a lamp are not safe unless the temperature may be controlled by a thermostat or by very frequent readings of the thermometer and careful regulation of the gas flame. If temperatures over 100° are desired, an ordinary copper-jacketed oven may be used, filling the jacket with toluol, xylol, aniline, or napthalene, according to the temperature desired, and placing a return cooler over the opening where the vapors escape.

Having been freed from the wash water as completely as possible by the suction pump (p. 13), or centrifugal machine (p. 18), the crystal mass or precipitate is spread in an even layer about three-quarters of an inch deep on a plate of ordinary double-thick window glass, taking care not to press the substance down, but to leave it as porous as possible. In the case of crystals or soluble precipitates the drying must be at as low a temperature as possible, and therefore they must be put in the *coolest part* of the closet and left there several hours before transferring to a warmer compartment.

When the crystals contain "water of crystallization," they should be dried at a temperature not exceeding 30° or 40°. The process is always attended with some difficulty. The crystals on top may effloresce or even fall to powder before the main part of the mass is nearly dry. This is especially liable to occur with such salts as sal soda, Glauber's salts, and borax, which contain large amounts of crystal water. Frequent turning over with a spatula may prevent this to some extent. Too high a temperature in the drying closet causes the crystals to melt down in their own "water of crystallization" or other

moisture present. When this happens the preparation is generally lost by running off the plate, and besides, may thus contaminate other substances in the closet. Consequently, it is always necessary to examine it at very frequent intervals, perhaps once in every ten minutes, while it is drying, until assured that neither efflorescence nor deliquescence is liable to occur. But it is generally best to dry such crystals in the centrifugal as far as possible, and then spread them out in the open air for an hour or two, frequently turning over the whole mass; or substances which deliquesce readily may be dried in desiccators over sulphuric acid or calcium chloride at the ordinary temperature of the room. A vacuum desiccator is very desirable for this purpose.

When a substance is to be dried at a high temperature, *e.g.* in the preparation of an anhydrous salt, it may be heated in a dry dish over the steam or hot-water bath until the "water of crystallization" is all expelled; it should then be transferred to a glass plate, as above described, and dried in the drying closet at 110°, or higher, if convenient. If the mass cakes together it may be necessary to pulverize it in a mortar and then return it to the closet until dry and powdery.

Some salts must be carefully protected from fumes or injurious gases during drying. This is especially true of silver, lead, and mercury salts, which are blackened by traces of hydrogen sulphide in the atmosphere of the drying closet.

In a few instances valuable preparations may be dried by spreading them on filter paper, which absorbs the excess of moisture, but this should not be done with large quantities of the salt. Unglazed earthenware plates ("biscuit ware") are occasionally convenient for absorbing moisture, especially in the case of organic substances containing oily or tarry admixtures; but in the following preparations there will seldom be occasion to use these special methods of drying.

In all cases the substance should be turned over two or three times while drying, and as soon as it is quite dry, removed from the closet and bottled while still warm.

DENSITY.

By density or specific gravity of a liquid is meant its relative weight compared with the weight of an equal volume of pure water. The determination of the density is one of the most frequent operations in chemical work. This may be done with a pyknometer when very exact results are required, but in technical operations sufficient accuracy for all practical purposes may be attained by the hydrometer. This is usually a glass instrument consisting of a cylindrical bulb weighted at the lower end and drawn out at its upper end to a long slender tube carrying a scale. (See Fig. X.) The graduations of this scale begin at the top and read down, the numerically greater reading being at the bottom, except in one instance — that of Baumé's scale for liquids lighter than water. Since the density of a liquid varies as its temperature changes, the scale is adjusted in every case to a certain definite temperature, usually about 15° C., at which determinations must be made.

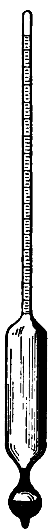

Fig. X.

When the hydrometer is put into a liquid, it sinks sufficiently to displace a volume of the liquid equal *in weight* to the weight of the instrument, and floats in an upright position. To determine the specific gravity of a liquid by means of a hydrometer, fill a hydrometer jar (Fig. XI) to the shoulder with the liquid to be tested and bring to the proper temperature by standing it in cold water, if the test is to be

made at 15° C. Insert the hydrometer, holding it by the tip of the stem, and allow it to sink slowly until the displacement of the liquid is just sufficient to support the instrument, and let it float free from contact with the jar. The temperature of the liquid should be taken again to be sure that no change has occurred. The scale reading should be taken as nearly as possible where the surface of the liquid touches the instrument, but owing to the meniscus formed at the junction of the liquid with the stem, this reading cannot always be seen exactly. However, a little care and practice will soon give sufficient accuracy for ordinary cases. In taking the gravity of liquids, especially if hot, to determine the crystallization point, the operation should be carried on as quickly as possible.

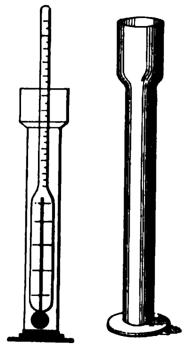

FIG. XI.

Should the hydrometer sink so deeply into the liquid that the scale is entirely below the surface, the density is less than the spindle is intended to measure, and one having smaller * numerical readings should be inserted and the test repeated. If, on the contrary, the spindle does not sink deep enough to bring the scale into the liquid, an instrument having greater numerical scale readings must be used.

Very accurate hydrometers may be purchased which afford exceedingly exact determinations, if properly used. A good instrument will give correct results to within 0.002 to 0.004 specific gravity, but this is seldom required for technical purposes. These instruments furnish a rapid and convenient method of determining approximate density.

Three systems of hydrometer scales are in common use, besides a large number of special scales intended to give one

* Baumé's hydrometer for liquids lighter than water is an exception. See p. 32.

particular factor in the density of the liquid; *e.g.* the per cent of alcohol in a mixture of alcohol and water, or the amount of sugar in a syrup, etc. But these special hydrometers are not called for in any of the preparations in this book.

Direct Specific Gravity Hydrometer.

This instrument is so constructed that the reading on its scale shows directly the density of the liquid as compared with pure water at the same temperature (15° C.). Its scale is adapted to liquids heavier or lighter than water. The point to which it sinks in pure water at 15° is marked 1.000 on the scale. As usually furnished, a set of these hydrometers consists of four spindles, the scale being thus divided into four sections. The first spindle, with gradations from 0.700 to 1.000, is for liquids lighter than water, and the others are for liquids heavier than water. The scale is usually divided about as follows: 1.000 to 1.300 on the second spindle, 1.300 to 1.600 on the third, and 1.600 to 2.000 on the fourth.

It will be observed that the gradations at the top of each spindle are wider apart than those at the bottom of the stem,* rendering the reading somewhat more difficult in dense liquids than in those of lighter gravity.

Twaddell's Hydrometer.

This is also a system of direct-reading hydrometers, and is a series of spindles (usually six in number), carrying gradations from 0 to 174. The reading in pure water at the temperature of 15.5° C. is taken as 0, and each subsequent raise of 0.005 sp. gr. is recorded on the scale as one additional division. Thus 10 Twaddell becomes 1.050 specific gravity. The grada-

* The explanation of this difference may be found in the larger works on physics.

tions on this scale also become closer together as the density increases, but as its total length is divided among six spindles, the reading is not so difficult even at the highest densities. The instruments are small, the gradations on each stem occupying about 3 linear inches, so that it may be used easily in an ordinary 100 cc. measuring cylinder. For these reasons, being easy to read, requiring but a small quantity of the liquid to be tested, and permitting a ready conversion of its readings into specific gravity by a very simple calculation, this is the most convenient hydrometer for ordinary factory or laboratory use. It is the instrument used in all determinations of density of liquids in this book, but in each case the corresponding specific gravity is inserted in parentheses.

The rule for the conversion of Twaddell readings into specific gravity is as follows: Multiply the readings obtained by .005 and add 1.000 to the product. Thus, 15 Twaddell becomes $1.000 + (15 \times .005) = 1.075$ specific gravity.

The readings of these instruments are corrected to a temperature of 15.5° C. (60° F.).

Unfortunately, Twaddell's scale is not adapted to liquids lighter than water, and for these specific gravity hydrometers may be used.

The use of the Twaddell hydrometer affords a ready means of determining the approximate quantity of water which should be added to a solution of a given gravity to produce one of a required density, the temperature remaining the same in both cases. Thus, given a solution at 50 Twaddell it is required to reduce it to 20 Twaddell. 1 cc. of solution at 50 Tw. contains as much dissolved matter as 50 cc. of the solution at 1 Tw.; or 20 volumes at 50 Tw. equal 50 volumes at 20 Tw. Hence, if the volume at 50 Tw. equal 1, the volume at 20 Tw. is $\frac{50}{20}$ of 1, or $2\frac{1}{2}$ times the volume at 50 Tw. Therefore, it is necessary to add $1\frac{1}{2}$ volumes of water.

BAUMÉ'S HYDROMETER.

This is an utterly unscientific instrument which is very largely used in technical work. Its readings are meaningless and bear no very direct relation to true specific gravity. Baumé dissolved 15 parts of pure salt in 85 parts of pure water at 12.5° C. Then he placed his instrument in this solution, and the point to which it sank was marked 15. The point to which it sank in pure water was marked 0. Then the distance between these points was divided into *fifteen equal parts*, and the entire stem marked off in divisions of this width. This produced an instrument for liquids heavier than water.

For liquids lighter than water the point to which the instrument sank in a 10% solution of salt was marked 0, and that to which it sank in distilled water was marked 10, the distance between these points being divided into 10 equal parts, and this gradation continued the entire length of the spindle. The 0 thus being placed at the bottom of the stem, the *lighter the gravity* of the liquid tested the *greater*, *numerically*, is the reading of the scale. For instance, a liquid reading 70 Bé. is of less density than one of 50 Bé., which, in turn, is lighter than water at 10 Bé.

To further complicate matters, the instrument makers appear to have become confused and produced instruments with erroneous scales. A test* made a few years ago discovered some thirty-four different scales, none of which were correct!

The conversion of Baumé readings to sp. gr. involves some calculation, and is usually accomplished by reference to tables.

There are two formulae for this conversion, one in common use in England and the other in America.

$$\frac{144.3}{144.3 - \text{Bé.}} \text{ (English.)} \qquad \frac{145}{145 - \text{Bé.}} \text{ (American.)}$$

*C. F. CHANDLER, "Proc. Nat'l Acad. Sciences." 1881.

PYKNOMETER.

This instrument will not be required for determining density in this work, but a description of it may not be out of place. It consists of a small bottle, having ground into its neck a tube drawn out to a capillary at its middle and enlarged at its upper end, which is closed by a stopper. (See Fig. XII.) The stopper is removed and the bottle filled brimful with the liquid to be tested; the tube is then inserted and pressed firmly home, the liquid displaced rising through the capillary to the enlarged part of the tube. The stopper is then loosely inserted and the bottle placed in a bath at the temperature at which the density is to be taken, and left there until its contents has reached that temperature. The stopper is then removed and the liquid in the reservoir removed by means of absorbent paper, until the level of the liquid recedes within the capillary to a fixed mark thereon. The stopper is then tightly inserted and the bottle removed from the bath, and after cleaning and drying its outside, allowed to stand until it reaches the normal temperature of the room. It is then weighed, and the density of the liquid is calculated from its known volume, previously determined by calibration.

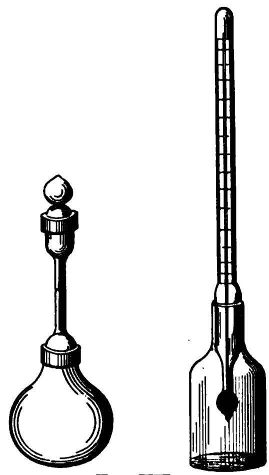

FIG. XII.

There are other methods of determining density, but their use will not be necessary in these preparations.

CALCINATION.

Calcination or ignition consists in heating a substance to a sufficiently high temperature to cause some change in its chemical composition or to expel some volatile constituent. It is carried out in crucibles, muffle furnaces, or reverberatories. The precautions to be taken are generally mentioned in connection with those preparations requiring the employment of this operation. Flat dishes of infusible clay can be had for the purpose of roasting small quantities of material. But if the charge requires much stirring, shallow pans of sheet iron may be used; or in some cases the charge may be spread directly on the floor of the muffle. For charges amounting to several pounds in weight, a small reverberatory or a revolving furnace will often be found convenient.

PULVERIZING.

It is almost always necessary to grind a mineral or other solid to a fine powder when it is to be dissolved or treated with any reagent. This is accomplished by passing it through a crusher and then through some kind of a grinding machine. Substances containing iron, or those from which iron impurities can be separated readily, are often powdered in a common iron mortar; but whenever iron would cause troublesome contamination, a porcelain mortar must be used. Large lumps may be broken by wrapping them in several thicknesses of stout paper and crushing them on an anvil by one or two sharp blows with a hammer. In this way very little contamination of the substance occurs. The small lumps so produced may be powdered in the mortar.

Soft material may be powdered by rolling on a board with an ordinary wooden rolling-pin or by pounding with a wooden mallet. For grinding considerable quantities of material, large porcelain mortars, eight inches or more in diameter, should be used, but for fine grinding of hard material, such as minerals, bones, etc., one of the various forms of pulverizing mills or crushing machines is recommended. Sometimes hard minerals may be pulverized by heating and dropping into cold water while hot. The coarse sand thus produced is then ground in the mortar.

GENERAL DIRECTIONS.

The following directions should be carefully read and remembered by the student, for they apply to all preparations and laboratory work. Disregard of any one of them usually causes loss of time or the spoiling of an experiment, and, frequently, broken dishes and apparatus.

1. Read each experiment through carefully before beginning the actual work, especially noting the precautions given. Make all calculations of quantities of material, and be sure that all figuring is correct, and that each step in the process is thoroughly understood before a gram of material is weighed out. Also see that the necessary apparatus is at hand, so that no needless delay may occur after the work is once started. Every preparation should be carried through to completion as rapidly as is consistent with careful work. In this way the liability to accident and contamination is much reduced. But the student should accustom himself to carrying on two or three preparations at once, so that no time may be lost while waiting for evaporation or crystallization.

2. The student should keep a neat and legible note-book in which to enter notes as the experiment progresses. *These must not be left to be "written up" later.* Enter all thermometer, hydrometer, burette, and scale readings, and all weights and measures of material, *as soon as made.* In nearly every preparation the reactions involved are given; using these and the tables in the appendix as bases, the student should determine how much material, reagent, water for solution, acids, etc., are needed and the amount of the theoretical yield, and enter the calculations *in full* in his notes. On completion of the experiment, enter the actual yield obtained. The quantities given at the beginning of each experiment are in most cases only approximate and intended as a guide. In all cases involving the use of crystallized salts, account must be taken of "water of crystallization," if any is present. Exact account must be kept of all materials added during the progress of an experiment, and their effect on the ultimate yield shown in the notes; also any accident which may occur and its probable effect on the result.

3. All dishes, flasks, beakers, and other apparatus should be marked with the student's name as soon as taken from the desk; also with the symbol of the substance contained in them. This is especially important when dishes are left containing solutions to evaporate or crystallize, or when two or three experiments are being carried on simultaneously.

4. All evaporating dishes should be weighed empty and the weight recorded in the note-book, as it is often desirable to calculate *e.g.* the amount of water contained in a solution after evaporation has proceeded to a certain point, or how much water has been evaporated out.

5. Much care as to cleanliness is very essential in chemical preparation work. Protect all preparations from dust, from spatterings from other work, and, as far as possible, from fumes

such as hydrogen sulphide or hydrochloric acid. All experiments in which copious fumes or vapors are evolved should be carried on under the hood, to avoid contaminating the air of the laboratory. Dishes and apparatus must be washed as soon as emptied and put away clean; they must also be washed and wiped clean and dry before using. Apparatus for general use in the laboratory, such as draining cones, hydrometer jars, measuring cylinders, centrifugal machines, presses, etc., *must be cleaned thoroughly immediately after using.* They should be examined in every case before using to see that they are clean.

6. In no case should a dish containing a heavy precipitate or undissolved substance in a liquid, be heated directly over the lamp, unless the contents be *actively* and *constantly* stirred. Otherwise the dish is almost certain to be broken. For the same reason an evaporating dish of more than 10 inches diameter should never be heated over a free flame, unless it contains at least 500 cc. of liquid; the outside of a dish must never be wet when put over a free flame, nor a cold liquid poured into a dry, hot dish nor into a very concentrated solution of a salt when boiling.

7. When digesting substances on the steam bath or over the lamp, be careful to replace the water evaporated from the solution, keeping the volume constant. Whenever it is necessary to add water to a hot solution, *always* add hot water, thus avoiding unnecessary cooling of the solution and also the risk of breaking the dish.

8. When effervescence occurs in dissolving or neutralizing a substance, as, for example, in adding an acid to a carbonate, always add the material slowly, in small portions at a time while stirring actively, waiting until the frothing subsides before adding the next portion. Neglect of these precautions generally results in sudden and violent effervescence, causing the contents of the dish to froth over, and entailing considerable loss.

9. Never throw away any mother liquors or residues until all valuable products have been extracted from them. If possible, keep all such material until the experiment is finished or until assured that no further use can be made of them. One of the chief aims of these preparations is to show how by-products may be utilized.

10. Have all bottles intended for the preservation of finished products *clean*, *dry*, and *cold* before putting the salts into them. A wet bottle will spoil a deliquescent preparation that has been days in drying, or salts containing water of crystallization may melt if put into a warm bottle.

PART II.

EXPERIMENTAL.

1. ALUMINUM CHLORIDE.

(Anhydrous.)

$AlCl_3$ (or Al_2Cl_6). M.W. = 133.5.

(*a*) Break up some pyrolusite into lumps as large as can be passed through the neck of a 1000 cc. round-bottom flask A, Fig. XIII, and fill it about one-quarter full. Through the two-

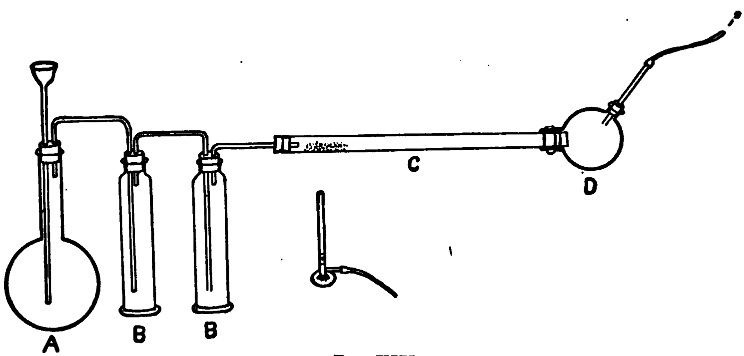

FIG. XIII.

hole rubber stopper pass a thistle tube and a glass delivery tube to connect with the first of the two wash bottles, as shown B, B, Fig. XIII. Put some water into the first bottle to absorb any hydrochloric acid gas which may come over, and concentrated sulphuric acid in the second to dry the chlorine

thoroughly. Join a piece of hard glass tubing C about 35 cm. long and $1\frac{1}{2}$ cm. internal diameter, to the second wash bottle with a piece of delivery tube and a cork, as shown in the figure.

Join the other end of this glass tube to the receiver D by means of a cork. From the smaller tubulature of the receiver, make a connection with the hood by means of a long piece of wide (10 mm.) delivery tubing, or lead this tube out of the window, where the escaping fumes of chlorine will do no harm. Into the combustion tube C put 5 grams of aluminum chips or turnings, which have been washed with ether or gasoline to remove oil, and then thoroughly dried. Place these chips near the end of the tube where the chlorine enters, the larger part of the tube being kept clear. By tapping the outside of the tube gently with the finger or a lead-pencil the chips will settle together, leaving a clear space above them for the free passage of chlorine gas.

When all the apparatus is tightly joined together, pour sufficient concentrated C. P. hydrochloric acid (sp. gr. 1.20) into the flask A to nearly cover the pyrolusite. Warm gently until a vigorous but steady evolution of chlorine gas is established. Allow the chlorine to pass through the apparatus until all the air is expelled, and then heat the combustion tube C containing the aluminum, at the end nearest the inlet for chlorine. The contents becomes red-hot, and then begins to glow and scintillate as the reaction takes place. The aluminum chloride sublimes over into the cool end of the tube, where it condenses as a pale yellow sublimate.

Continue the heating as long as the residue glows. When on prolonged heating it becomes black, remove the lamp and allow the tube to cool somewhat, while the stream of chlorine continues to pass through the apparatus. Then disconnect the combustion tube while still warm, and rake out the aluminum

chloride with a glass rod, being careful not to mix any of the residue with it. The aluminum chloride should be received at once into a perfectly dry bottle, which has been previously weighed with its stopper. All moisture *must* be avoided, and the transfer from the tube to the bottle must be made as quickly as possible after disconnecting the tube. The combustion tube C may be recharged at once with another 5 grams of aluminum and the process repeated, first emptying the spent acid * from the chlorine generator and replacing it with fresh acid. The pyrolusite should last through several rechargings with acid. After several rechargings with aluminum, or at the end of the experiment, the fine deposit of aluminum chloride in D may be raked out with a glass rod and put with the other.

Reaction:

$$Al + Cl_3 = AlCl_3.$$

The yield from 10 grams of metallic aluminum is from 35 to 38 grams of pure aluminum chloride. The residue in the tube consists of aluminum oxide and impurities in the metal.

The bottle containing the preparation must be very tightly stoppered, and care must be exercised in opening it, since very considerable pressure is accumulated, probably due to the hydrochloric gas set free by the action of the moisture in the air upon the aluminum chloride.

(*b*) For the preparation of larger quantities of the anhydrous salt, to be used in organic syntheses by Friedel and Crafts' method, † the author has found the process devised by Gattermann ‡ exceedingly satisfactory. This does not yield quite so light-colored a product as does the preceding method, but it is sufficiently pure for synthetical work.

* This solution of manganous chloride should be preserved and used in the preparation of that salt, as described on p. 135.

† Compt. Rend. **86**, 1368 ; **92**, 833.

‡ Ber. **1892**, 3521.

Put 1500 cc. of concentrated hydrochloric acid (sp. gr. 1.20) into a 3000 cc. round-bottom flask A, Fig. XIV. Pass the stem of a 200 cc. separatory funnel through the rubber stopper, the point of the stem being about two inches below the stopper, and so arranged that concentrated sulphuric acid (sp. gr. 1.84) may be *dropped* into the hydrochloric acid without its running down the sides of the flask. The glass delivery tube must be connected closely with the two gas wash bottles B, B, Fig. XIV, each containing concentrated sulphuric acid (sp. gr.

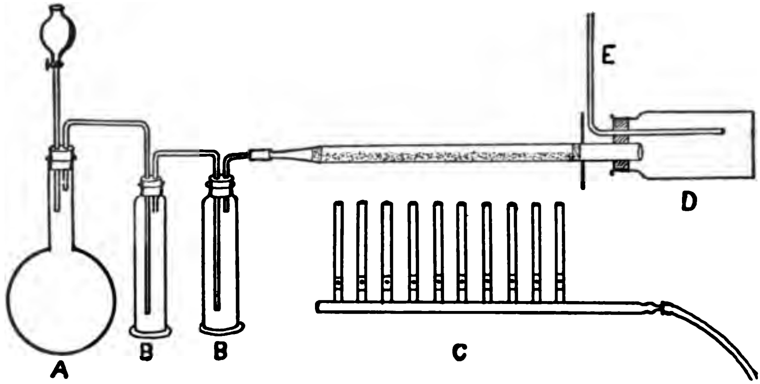

FIG. XIV.

1.84). Select a combustion tube of large diameter (18 mm.) and about 10 cm. longer than the combustion furnace C to be used. Draw out one end of this tube in the blast lamp to a taper about 15 cm. long and 5 mm. diameter at the small end. Pass the other end of the tube through the cork of the bottle D, fitting it snugly and allowing the end to extend only 2 to 3 mm. into the bottle. Through this same cork pass an outlet tube E of soft glass, having a diameter of 1 cm. and extending to within 3 cm. of the bottom of the bottle. The free end of this outlet tube should be extended into the hood or out of doors, and if possible, so arranged that a glass rod or a brass or copper

wire may be passed through it to push back into the bottle any deposit of aluminum chloride which might tend to clog the outlet tube.

Put a loose plug of asbestos into the combustion tube at the base of the drawn-out end, and then pour in aluminum turnings (previously freed from oil) till the tube is $\frac{3}{4}$ or $\frac{7}{8}$ full. Put in another loose asbestos plug, and lay it on a table or hold it horizontally in the hand, and tap it gently till a clear passage is secured, over the chips, throughout the whole length of the tube. Place the tube in the combustion furnace C, with the clear passage uppermost, and join the drawn-out end with the gas wash bottle B by means of a short rubber connection. Bring the bottle D up in a horizontal position so that its mouth is closed tightly by the cork carrying the combustion tube and the exit tube. It is best to so arrange the cork that both tubes shall lie in the same horizontal plane about on a line with the median section of the bottle. (In the figure these are shown in the vertical plane.) When all is tight and ready, put some concentrated sulphuric acid (sp. gr. 1.84) into the separatory funnel, and let it drop rather rapidly into the hydrochloric acid in the flask A. After about 75 to 100 cc. have been thus introduced, the temperature of the flask begins to rise, and soon a copious evolution of hydrochloric acid gas begins, which can easily be controlled by regulating the dropping of the sulphuric acid. Allow the strong stream of hydrochloric acid gas to run through the apparatus for from 10 to 15 minutes until *all the air is expelled from the bottles* which is usually shown by the escape of acid fumes into the hood at the open end of the outlet tube. *Not until now* should the burners of the furnace be lighted, otherwise an explosion may occur. Heat the tube slowly, burning a low flame on all the burners, but presently raise it to a low red heat at the inlet end, and keep it so until the metal has nearly all been converted into aluminum

chloride and sublimed away. Turn the burners on by twos and threes as the metal slowly burns away until all of it has been converted and passed over into the bottle. Be careful not to heat the aluminum hot enough to cause fusion into globules, for then the action of the hydrochloric acid gas becomes exceedingly slow and tedious. The stream of gas must be fairly rapid, and the outlet tube must not be allowed to become clogged with a deposit of aluminum chloride. It is generally necessary to heat the tube between the furnace and the bottle D with a Bunsen lamp. The cork may be protected from burning by an asbestos plate, perforated and slipped on the combustion tube before passing this through the cork.

Should the stream of hydrochloric acid gas passing through the drying bottles suddenly cease while the sulphuric acid is being rapidly dropped in, clogging may be suspected at once. By disconnecting the short rubber tube between the second bottle B and the combustion tube, it may easily be determined if such is the case, or if the hydrochloric acid solution has become exhausted. In the former instance clean the outlet tube with a copper or brass wire or glass rod, or clean the combustion tube by heating rapidly where the clogging is supposed to be. If these means fail to clear the apparatus, it is best to stop the experiment and determine the yield of aluminum chloride, such as it may be. Partially corroded aluminum turnings do not seem to work satisfactorily when placed in the furnace a second time.

As soon as the experiment is ended, disconnect the bottle containing the aluminum chloride from the perforated cork at once, while still warm, scrape the chloride adhering to cork, combustion tube, and outlet tube into the bottle, stopper or cork tightly, and place it in a desiccator over concentrated sulphuric acid for keeping.

The advantages of this process are the easy control of the gas stream and the usually better yield than from (*a*). Under favorable conditions from 190 to 200 grams of aluminum chloride may be obtained from 50 grams of aluminum.

A modification of this apparatus may sometimes be employed by substituting for the flask and separatory funnel an ordinary Kipp's generator, charged with sublimed ammonium chloride in lumps and with concentrated sulphuric acid.

Properties:

Anhydrous aluminum chloride is a white crystalline substance, taking a yellow tinge when traces of iron are present. It has a strong odor of hydrochloric acid. When exposed to the air it gives off hydrochloric acid, attracts moisture, and finally deliquesces. It is soluble in 1.43 parts of water at 15° C. and also somewhat soluble in alcohol and ether. It sublimes unchanged below incipient red heat.

It is frequently used in organic synthetical work to assist in the condensation of hydrocarbons, in which process water is eliminated. For this the aluminum chloride must be freshly prepared and as free from moisture as possible.

Owing to slight decomposition on standing, by which gaseous hydrochloric acid is set free, considerable pressure is generated in the bottles in which the salt is kept. Hence, care should always be exercised in opening the bottles, especially after standing for some days, lest an explosion should occur.

Bunsen, Jahresbericht über die Fortschritte der Chemie, **1865**, 181.
Mabery, Ber. **1889**, 2658.
Warren, Chem. News, **1887**, 55–192.
Gattermann, Ber. **1892**, 3521.

2. ALUMINUM CHLORIDE.*

(Crystallized.)

$AlCl_3.6\,H_2O$. M.W. = 241.5.

Prepare moist aluminum hydrate according to the method given on page 47, or from a solution of alum or aluminum sulphate by precipitating with carbonate or bicarbonate of sodium. Wash the hydrate free from soluble salts, and dissolve it in dilute hydrochloric acid, using a slight excess of the acid over the amount necessary for complete solution. Evaporate it to crystallization on the water bath. Crystals having $6\,H_2O$ are obtained from the acid solution.

Crystallized aluminum chloride is prepared technically by decomposing a solution of aluminum sulphate with barium or calcium chloride.

Properties:

The crystallized salt containing $6\,H_2O$ is soluble in 0.25 parts of water at 15° C. The saturated solution at the same temperature has a gravity of 70.4 Tw. (1.352 sp. gr.) and contains 41% of anhydrous salt. The salt decomposes when its *aqueous solution* is evaporated to dryness and heated gently.

The solution is sometimes used as a disinfectant.

* BONSDORFF, Pogg. Ann. **27**, 279.
VON HAUER, J. pr. Chemie, **80**, 220.

3. ALUMINUM HYDRATE.

$Al(OH)_3$. M.W. = 78.

$$Al_2O_3.3\ H_2O = Al_2(OH)_6 = 2\ Al(OH)_3.$$

Take of

Cryolite (powdered),	1400 gr.
Calcium carbonate (powdered),	2000 "

Pulverize the cryolite as fine as possible, and mix it thoroughly with fine marble dust according to the molecular proportions required in the reaction (see below). Heat the mixture at a high temperature for ½ or ¾ of an hour in a platinum dish or clay crucible. The mass sinters together, and, after cooling and removing it from the crucible, must be finely pulverized and then extracted with boiling water. Traces of calcium salt held in the solution may be precipitated by adding a small quantity of sodium carbonate solution. Precipitate the filtered solution of sodium aluminate by passing a stream of carbon dioxide into it while it is still hot, or by adding a solution of sodium bicarbonate. Wash the precipitated aluminum hydrate with plenty of hot water by decantation (p. 20), repeating the process several times until the wash water is free from sodium carbonate.*

The precipitated aluminum hydrate should be a white earthy powder, free from all impurity except a trace of sodium carbonate. This may be removed by digesting the aluminum hydrate with a solution of aluminum chloride, followed by repeated washings with water. The sodium aluminate solution may also be precipitated by carefully adding dilute hydrochloric

* The sodium carbonate may be recovered from the filtrate and first wash water by evaporation (p. 21).

acid until the liquid is just acid. Wash the precipitated hydrate with warm water as above described. Dry in the hot closet.

Reactions:

$$Na_3AlF_6 + 3\ CaCO_3 = Al(ONa)_3 + 3\ CaF_2{}^* + 3\ CO_2.$$
$$2\ Al(ONa)_3 + 3\ CO_2 + 3\ H_2O = 2\ Al(OH)_3 + 3\ Na_2CO_3.$$

Properties:

Aluminum hydrate is a paste-like translucent mass when precipitated from solution by means of ammonia, but when thrown down by carbon dioxide or sodium bicarbonate the precipitate is more or less granular. It may be used as the basis of other aluminum salts. It is dissolved by an excess of caustic alkalies forming salts known as aluminates (see above) which are very unstable bodies.

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4. ALUMINUM SULPHATE.

$Al_2(SO_4)_3 \cdot 18\ H_2O.$ M.W. = 664.8.

(*a*) Take of

Bauxite,	500 gr.
Sodium carbonate,	1500 "

Thoroughly mix 1 part of finely ground bauxite with 3 parts of anhydrous sodium carbonate, put a small quantity of the mixture into an iron crucible (No. 6), and heat to fusion. A violent evolution of carbonic acid occurs; as soon as the fusion becomes quiet add a little more of the mixture, and allow it to

* The calcium fluoride may be washed and dried and used as a blowpipe flux, or for the preparation of hydrofluoric acid.

come to a quiet fusion, repeating this till the crucible is $\frac{3}{4}$ full. Heat the fusion at a bright red heat for about 2 hours, and then pour it into a shallow iron pan to cool. Grind the cold mass very fine, and extract it with distilled water for about an hour. Allow it to settle, and filter it. Add a little more water to the residue, and extract again. The filtrate is a dark-colored solution containing sodium aluminate and some suspended matter which deposits on standing over night. Decant or filter this solution, and bring it to the boil. While boiling add sodium carbonate in small quantities until the iron is *all precipitated*, as shown by tests filtered off, acidified with hydrochloric acid, and potassium ferrocyanide added. Then filter or decant. Precipitate the aluminum hydrate with sodium bicarbonate as described on page 47, taking care not to add an excess of the reagent. Wash the precipitate with hot water until free from sodium salts. Dissolve the precipitated aluminum hydrate in moderately dilute sulphuric acid, and evaporate to a density of 40 Tw. (1.2 sp. gr.) in the hot solution and allow it to crystallize. No excess of acid should be used, for that would cause the product to be sticky. It is better to have a small amount of the aluminum hydrate remain undissolved by the acid even after long standing.

Bauxite is a more or less pure mineral containing iron and aluminum hydrates. The composition is $Al(OH)_3 + xFe(OH)_3$. The quantity of iron present varies much.

Reactions:

$$2\,Al(OH)_3 + 3\,Na_2CO_3 = 2\,Al(NaO)_3 + 3\,CO_2 + 3\,H_2O.$$
$$Al(NaO)_3 + 3\,NaHCO_3 = Al(OH)_3 + 3\,Na_2CO_3.$$
$$2\,Al(OH)_3 + 3\,H_2SO_4 + 12\,H_2O = Al_2(SO_4)_3 + 18\,H_2O.$$

The solution of sodium aluminate may be precipitated by passing in carbonic acid gas as described on page 47. The solu-

tion of aluminum sulphate may be evaporated to a thick syrup and allowed to solidify on cooling, in which case a product, known as "concentrated alum," similar to porous alum, is obtained.

(*b*) From cryolite:

Take of

Cryolite (powdered),	1000 gr.
Quick lime (powdered),	800 "
Water,	4000 cc.

Slake the lime in a 2-gallon earthen-ware crock by wetting with 300 cc. of water. When slaked to a soft powder, add the remainder of the water, and stir to a thin cream. Stir in the finely powdered cryolite, and boil for 6 or 8 hours, by means of a lead steam coil in the crock, replacing the water as it evaporates. The mixture becomes yellowish brown, owing to the iron present. Filter on a cloth bag (p. 10), and wash several times until the density of the wash water is 2° Tw. (sp. gr. 1.010). Combine the filtrate and the wash waters in a 16-inch evaporating dish, and evaporate to a convenient bulk of perhaps 3 liters. Purify this solution (of sodium aluminate), and prepare aluminum sulphate from it as directed in (*a*).

Reaction:

$$AlF_3 \cdot 3\,NaF + 3\,CaO = Al(NaO)_3 + 3\,CaF_2.$$

(*c*) Cryolite may be decomposed by heating with powdered limestone in a crucible according to the molecular proportions of the equation:

$$AlF_3 \cdot 3\,NaF + 3\,CaCO_3 = Al(NaO)_3 + 3\,CaF_2 + 3\,CO_2.$$

Treat the ignited mass as in (*a*).

Properties:

Aluminum sulphate is soluble in 1.2 parts of water at 15° C. and is much more soluble in hot water. When carefully heated in the air it loses its water of crystallization and forms a porous mass (porous alum). The salt shows an acid reaction with litmus. The following table * shows the density of solutions of aluminum sulphate:

	15° C.	25° C.	45° C.
5% $Al_2(SO_4)_3 \cdot 18\,H_2O$	1.0569	1.0503	1.0356
10% "	1.1071	1.1022	1.0850
15% "	1.1574	1.1522	1.1346
20% "	1.2074	1.2004	1.1801
25% "	1.2572	1.2483	1.2295

100 parts of water dissolve † at

0°	10°	20°	30°	
31.3	33.5	36.15	40.36	parts of $Al_2(SO_4)_3$.
86.85	95.8	107.35	127.6	" " $Al_2(SO_4)_3 + 18\,H_2O$.

40°	50°	60°	70°	
45.73	52.13	59.09	66.23	parts of $Al_2(SO_4)_3$.
167.6	201.4	262.6	348.2	" " $Al_2(SO_4)_3 + 18\,H_2O$.

80°	90°	100°	
73.14	80.83	89.11	parts of $Al_2(SO_4)_3$.
467.3	678.8	1132.	" " $Al_2(SO_4)_3 + 18\,H_2O$.

* REUSS, Ber. **17**, 2888.
† POGGIALE, Ann. Chim. Phys. [3] **8**, 467.

5. ALUM.

$K_2SO_4, Al_2(SO_4)_3 \cdot 24\ H_2O$ M.W. = 948.
or $KAl(SO_4)_2 \cdot 12\ H_2O$.

$(NH_4)_2SO_4, Al_2(SO_4)_3 \cdot 24\ H_2O$ M.W. = 906.
or $(NH_4)Al(SO_4)_2 \cdot 12\ H_2O$.

Alum is made from the aluminum sulphate derived from cryolite (p. 50), or from bauxite (p. 48). Dissolve the given weight of aluminum sulphate in the proper quantity of hot water (see SOLUTION, p. 4), then add the calculated weight of potassium or ammonium sulphate dissolved in hot water, and stir the mixture thoroughly. On cooling, the potash or ammonia alum separates out in clear octahaedral crystals. Evaporate the mother liquor to obtain more of the alum. Purify by recrystallizing once or twice from distilled water. Dry the crystals in the coolest part of the drying closet, examining them frequently.

Properties:

Alum is not readily soluble in cold water. 100 parts water at *

0°	dissolve	3.90 parts $K_2Al_2(SO_4)_4 \cdot 24\ H_2O$ or	5.22 parts $(NH_4)_2Al_2(SO_4)_4 \cdot 24H_2O$.
10°	"	9.52 " " "	9.16 " "
20°	"	15.13 " " "	13.66 " "
30°	"	22.01 " " "	19.29 " "
50°	"	44.11 " " "	36.51 " "
80°	"	134.47 " " "	103.08 " "
90°	"	209.31 " " "	187.80 " "
100°	"	357.48 " " "	421.90 " "

* POGGIALE, Ann. Chim. Phys. [3] 8, 467.

6. CHROME ALUM.

$K_2SO_4, Cr_2(SO_4)_3 \cdot 24\,H_2O$ M.W. = 999.
or $KCr(SO_4)_2 \cdot 12\,H_2O$.

Commercial chrome alum is chiefly obtained as a by-product in the manufacture of artificial alizarine; but this contains various impurities, such as lime salts, etc. To prepare a pure alum:

Take of

Potassium bichromate,	100 gr.
Sulphuric acid, 168 Tw. (1.84 sp. gr.),	123 "
Water,	220 "
Starch,	24 "

Dissolve the bichromate of potash in the acid and water, and add the starch very slowly. A violent action takes place, and the mixture becomes very hot. The temperature must remain high during the reaction, but no external heating should be used as long as the reaction will proceed without it. The solution becomes a bluish green color; if it is olive green the bichromate is not all decomposed, and it may be necessary to heat it.

The solution may not crystallize well on cooling, but a few crystals dropped into the liquor will often cause crystallization.

Reaction:

$$2\,K_2Cr_2O_7 + 8\,H_2SO_4 + 6\,H_2 + 34\,H_2O = 2\,K_2SO_4, Cr_2(SO_4)_3 \cdot 24\,H_2O.$$

The bichromate of potassium and sulphuric acid may be reduced by a stream of sulphur dioxide passed into the solution.

$$K_2Cr_2O_7 + H_2SO_4 + 3\,SO_2 + 23\,H_2O = K_2SO_4,Cr_2(SO_4)_3 \cdot 24\,H_2O.$$

Properties:

Chrome alum forms dark purple crystals which are soluble in 7 parts of cold water. The solution is a reddish blue color, but if heated above 70° C. it becomes green. The crystals effloresce on exposure to the air, or when dried at 25 to 30° C. When heated to 350° C. they lose all their crystal water, but if heated above this temperature the residue becomes insoluble in water.

Specific gravity * of chrome alum solution (violet modification) at 15° C.

Sp. gr.	% $K_2Cr_2(SO_4)_4 \cdot 24\,H_2O$.
1.02725	5
1.05500	10
1.08350	15
1.0985	Sat. solution at 15°.

7. AMMONIUM BICARBONATE.†

NH_4HCO_3 (acid carbonate). M.W. = 79.

(*a*) This salt is most readily obtained by dissolving commercial carbonate in water at 50° C. and treating it with carbon dioxide from a Kipp's apparatus while cooling. The delivery

* Gerlach, Zeit. anal. Chem. **28**, 497.

† Dibbits, J. pr. Chem. [2] (1874) **10**, 434. Rose, Pogg. Ann. **46**, 395. Deville, Ann. Chim. Phys. [3] **40**, 87.

tube for the carbon dioxide must be moderately wide to prevent clogging. Filter the crystalline mass of bicarbonate which has separated out, on a Büchner funnel at once (p. 14), and dry for several days in a desiccator over sulphuric acid.

(*b*) The salt may also be prepared by passing carbon dioxide into a flask containing concentrated ammonia water (sp. gr. 0.900) while cooling the flask with running water. The bicarbonate crystallizes out from the solution. Neither of these methods yields a product entirely free from carbamate.

Reactions:

$$(a)\quad (NH_4)_2CO_3 + CO_2 + H_2O = 2\,NH_4HCO_3.$$

$$(b)\quad NH_4OH + CO_2 = NH_4HCO_3.$$

Properties:

Ammonium bicarbonate is quite soluble in water, 100 parts of which at

0°	dissolve *	11.9	parts of	crystallized salt.
10°	"	15.85	"	"
15°	"	18.3	"	"
20°	"	21.0	"	"
25°	"	23.9	"	"
30°	"	27.0	"	"

The solution loses carbonic acid at ordinary temperatures or on standing in the air. The dry salt is stable and odorless, but at 60° C. decomposes into ammonia, water, and carbonic acid.

* DIBBITS, J. pr. Chem. [2] **10** (1874), 439.

8. AMMONIUM CARBONATE.

$(NH_4)_2CO_3 + H_2O$ (neutral salt *). M.W. = 114.

(*a*) Digest 1 part of commercial ammonium carbonate (*sal volatile*) with 4 parts of concentrated ammonium hydrate for 2 days in a closed flask at a temperature of 20–25° C. The contents of the flask become a crystalline solid, which is the neutral ammonium carbonate.

(*b*) $(NH_4)_2CO_3 \cdot H_2O$.

Dissolve commercial ammonium carbonate in warm dilute ammonia solution in a closed flask. Let it cool, and the carbonate crystallizes. If large excess of free ammonia is present the crystals are small, but in moderate excess they are large.

The crystals are obtained by pouring the contents of the flask into a straining cloth or bag (p. 10) and pressing quickly.

The pure salt cannot be prepared by passing carbonic dioxide into ammonia water, since more or less carbamate of ammonia is formed.

Ammonium carbonate is soluble in an equal weight of water at 15° C., and decomposes on exposure to the air or on heating to 50–60° C.

$$(NH_4)_2CO_3 = NH_4HCO_3 + NH_3 + H_2O.$$

* Kolbe, Handwörterbuch d. Chemie. Suppl. 157. Divers, J. Am. Chem. Soc. 1870 (8), 176.

9. AMMONIUM CHLORIDE.

NH_4Cl. M.W. = 53.5

Take of

Sal ammoniac,	1000 gr.
Distilled water (hot),	1800 cc.

For the preparation of pure ammonium chloride, use the commercial sublimed *sal ammoniac*. This is usually made by subliming crude crystallized ammonium chloride prepared from gas liquor and hydrochloric acid. The sublimed salt is of a crystalline fibrous structure and has a translucent white appearance. Being sublimed in iron pots, its chief impurity is iron chloride. To purify from iron, crush the sal ammoniac to lumps the size of a walnut, and dissolve in the proper quantity of hot distilled water (p. 4). When all dissolved, add about 25 cc. of strong chlorine water for each kilo of salt used, and boil for 20 minutes or half an hour. The solution generally becomes a marked yellow color as the iron is oxidized to ferric chloride. Then carefully add ammonia water to the hot solution until a distinct odor of ammonia persists after stirring. Continue the boiling until the odor of ammonia has become very faint or has entirely disappeared. Filter off a few cc., and test for iron with both ferrocyanide and ferricyanide of potassium. If iron is found, repeat the treatment with chlorine water and ammonia till it is all precipitated. Filter hot, either on paper in a 6 or 8-inch funnel, or by upward filtration (p. 15). Evaporate the solution till saturated, and allow to cool and white needle-like crystals form. Separate these from the mother liquor by straining in the porcelain drainer or on a Büchner funnel (p. 14), no filter cloth or paper being necessary. Evaporate the mother liquor to further concentration,

and a second crop of crystals will separate ; repeat the process until all the salt is obtained. After draining the crystals as dry as possible, spread them on glass plates in layers about one-half inch thick, and dry for 1 or 2 days in the drying closet at the lowest temperature. Then turn the crystal mass over on the plates, and dry for another day in the hotter part of the closet. The yield is about 95% of pure NH_4Cl.

If desired the purified solution may be evaporated to dryness directly on the steam or water bath, but the product will not be so well crystallized and attractive appearing. Moreover, some loss may occur by the volatilization of the ammonium chloride if heated too much. The boiling solution should be concentrated to 17.6 Tw. (1.088 sp. gr.) to form the best crystals.

Chlorine gas may be employed to oxidize the iron instead of chlorine water as directed, but the gas must be passed into the solution *for a short time only.* Prolonged treatment of the solution, especially when cold, might result in the formation of the dangerous nitrogen chloride. But chlorine water will be found to be more convenient to use.

For a chemically pure product, such as is occasionally required in analysis, C. P. hydrochloric acid may be neutralized by pure ammonia in the same way as described for ammonium nitrate (p. 61). Recrystallize the product from distilled water.

The crystallized *muriate of ammonium* of commerce usually contains sulphates of iron and calcium. To remove these, treat the hot solution of the salt with barium chloride and filter. Boil the filtrate with ammonium carbonate or oxalate solution to remove excess of barium and calcium. Filter and acidify the filtrate with hydrochloric acid, and neutralize with ammonia. If iron is still present, remove it by treating with chlorine water and ammonia as above.

Sodium salts are sometimes present in the technical product, and there is no economical way of separating them completely from the ammonium chloride.

Properties:

Ammonium chloride is a pure white or translucent crystalline mass, odorless at ordinary temperatures and volatile when heated. It is very soluble, dissolving in 2.7 parts of cold water and in less than 1.3 parts of hot water.

100 parts of water at

0° C.	dissolve	28.40	parts	NH_4Cl.*
20° "	"	37.28	"	"
50° "	"	50.60	"	"
100° "	"	72.80	"	"
110° "	"	77.24	"	"

The boiling * point of a saturated solution is about 115.8°, and at this temperature 100 parts of water dissolve about 88.9 parts of NH_4Cl.

The specific gravity † of ammonium chloride solutions at 19° C. is as follows:

10%	NH_4Cl	— 1.0293.
20%	"	— 1.0579.
25%	"	— 1.0714.
30%	"	— 1.085.

The solution should give no tests for phosphoric or sulphuric acids, nor should hydrogen sulphide, ammonium sulphide, ammonium oxalate, or ammonia show any impurity.

* ALLUARD, Ann. Chem. Pharm. **133**, 292. *Ibid.*, Compt. Rend. **59**, 500.
† SCHIFF, Ann. Chem. Pharm. **110**, 74.

10. AMMONIUM IODIDE.*

NH_4I. M.W. = 145.

Take of

Potassium iodide,	252 gr.
Ammonium sulphate,	100 "
Water,	275 cc.

Mix a hot saturated solution of the theoretical quantity of potassium iodide dissolved in one-half its weight of water, with the given amount of ammonium sulphate dissolved in $1\frac{1}{2}$ times its weight of boiling water. After cooling, add alcohol equal to 15% of the total quantity of water used, and let stand 12 hours. Filter off the precipitated potassium sulphate. Evaporate the filtrate, occasionally adding ammonia water containing some alcohol, until crystallization begins, and then allow it to cool. Extract the crystals of potassium sulphate with dilute ($\frac{1}{5}$) alcohol, and after combining the filtrates evaporate to crystallize the ammonium iodide.

Reaction:

$$(NH_4)_2SO_4 + 2\ KI = K_2SO_4 + 2\ NH_4I.$$

Properties:

Ammonium iodide crystallizes in cubes and deliquesces in the air. It should be preserved in a dark place, as light decomposes the salt, causing it to turn brown. This coloration may be removed by dissolving in distilled water, treating the solution with ammonium sulphide, filtering, and evaporating the filtrate on the steam bath, to crystallize. It is readily soluble in alcohol. The aqueous solution becomes yellow on standing, owing to decomposition and separation of iodine. One part of the salt dissolves † in 0.60 part of water.

* Jacobson, Chem. Centralb. **1864**, 192.
† Eder, Dingl. J. **221**, 89.

11. AMMONIUM NITRATE.

NH_4NO_3. M.W. = 80.

Take of

Nitric acid C. P. conc. 68 Tw. (1.340 sp. gr.), 1100 cc.
Ammonia water, conc. or ammonium carbonate, } a sufficient quantity.

Ammonium nitrate is usually prepared by neutralizing dilute nitric acid with ammonium hydrate or ammonium carbonate. It is best to measure the acid and ammonia each into a narrow-neck flask from which they may be poured as needed. Put 100 cc. of water and 50 cc. of the nitric acid into an evaporating dish of sufficient capacity to hold the solution of the entire amount of the ammonium nitrate to be made. Drop in a piece of litmus paper about ¼-inch square, and then add concentrated ammonia very slowly, with constant stirring, until the litmus shows *just neutral* reaction. Add another 50 cc. of acid, and again bring to neutrality with ammonia, and so on until the bulk of the liquid becomes 600 to 700 cc. Then the amount of acid added at one time may be increased to 100 or 150 cc., until the entire quantity taken for the preparation has all been neutralized. [J. W. Smith, private communication.]

Since the heat of the reaction is very intense, the dish must be kept cool by placing it in a tub or sink full of cold water. If the temperature is not kept down, volatilization of the ammonia, and, in the case of concentrated solution, possible decomposition of the product will occur. Base all calculations in this preparation on the amount of nitric acid, as a small amount of the ammonia is unavoidably lost during the neutralization; but if the solution is always kept *acid* or barely neutral, this loss is very small. At the last, bring the solution just to the point of alkalinity, and allow it to stand and cool

completely. It generally happens that a brown sediment will separate out, consisting, probably, of traces of iron and tarry matter from the ammonia. Filter the solution, and evaporate to saturation or to dryness in the warm closet, or bring to a density of 47 Tw. (1.235 sp. gr.) in the hot solution and allow it to cool, and long crystals of ammonium nitrate will separate out. When free from adhering mother liquor, dry them in the warm closet. If crystals are not especially desired the solution may be evaporated directly to dryness, in which case a hard cake of crystalline structure is obtained. The yield should be at least 95% of the theory.

Reaction:

$$NH_4OH + HNO_3 = H_2O + NH_4NO_3.$$

Since water is formed in the reaction, the product remains in solution until after concentration. For this reason also it is unnecessary to add more water to the acid after the first 100 cc., because the water thus formed, together with that contained in the ammonia, acts as sufficient diluent to the solution.

Commercial samples often contain sulphate, which may be removed by adding barium nitrate, and, after filtering, treating with ammonium carbonate and ammonium hydrate and then warming. Filter again, and add nitric acid until just neutral.

When heated in a platinum crucible no appreciable residue should be left.

Properties:

Ammonium nitrate melts at 152° * C., and decomposes at 210° C. By very careful heating at 190–200° C.† it may be sublimed. When dissolved in water considerable heat is absorbed, and hence it is sometimes used for cooling mixtures.

* BERTHELOT, Compt. Rend. **82**, 932.

† GRAHAM-OTTO, Anorganische Chemie.

It finds occasional use in analytical work to assist in the carbonization of filter paper during ignition. It is chiefly employed in the arts to prepare nitrous oxide, by heating in a retort.

$$NH_4NO_3 = 2\ H_2O + N_2O.$$

But care must be taken that the heating be slow and to a moderature temperature, otherwise an explosion may occur.

Ammonium nitrate is soluble in one-half its weight of water at 18° C.

100 parts of water * at

0° C.	dissolve	97	parts	NH_4NO_3.
10° "	"	139	"	"
20° "	"	185	"	"
25° "	"	210	"	"
30° "	"	238	"	"
40° "	"	298	"	"
50° "	"	365	"	"
60° "	"	441	"	"
70° "	"	526	"	"

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12. AMMONIUM OXALATE.

$(NH_4)_2C_2O_4 \cdot H_2O$. M.W. = 142.

Take of

Oxalic acid (purified),	1000 gr.
Ammonia (sp. gr. 0.910), about	1200 cc.
Water (distilled),	3000 "

Put the oxalic acid into a 14-inch evaporating dish, and add 2 liters of hot water. Stir until the acid is dissolved, heating on the steam bath if necessary. Dilute the ammonia with 1

* MULDER, Scheik. Verhand. **1864**, 95.

liter of cold water, and add this to the oxalic acid solution, in small portions at a time, while stirring actively. A precipitate of acid ammonium oxalate may appear when about $\frac{1}{4}$ of the ammonia has been added, but this will redissolve after a considerable portion of the ammonia has been added.

When the liquid acquires a distinct odor of ammonia after thorough stirring and has become strongly alkaline to litmus paper, filter if necessary, and evaporate until a pellicle appears on the surface. Add a few cc. of hot distilled water until this just redissolves, test again with litmus, and, if not alkaline, add a few drops of concentrated ammonia and cover the dish, putting it in a cool place to crystallize. Decant the mother liquor, and drain the crystals in a covered funnel or use the centrifugal machine. Dry in the warming oven at a moderate temperature, frequently turning the mass over while drying. On further evaporation the mother liquor will yield more crystals.

An excess of ammonia must be used, as some is lost by volatilization, owing to the heat of the combination.

Instead of ammonia liquor, the commercial carbonate of ammonia may be used, but in this case care is necessary to prevent loss through effervescence and foaming of the liquid. The dry carbonate may be added in small lumps directly to the solution of oxalic acid, until the latter is neutral.

Reaction:

$$C_2H_2O_4 \cdot 2\ H_2O + 2\ NH_3 = (NH_4)_2C_2O_4 \cdot 2\ H_2O.$$

Properties:

Ammonium oxalate forms needle-like crystals soluble in about 3 parts of water at 25° C. and yielding a neutral solution. For use as an analytical reagent, the salt must give no test for sulphuric acid when hydrochloric acid and barium chloride are

added. Neither hydrogen sulphide nor ammonium sulphide and ammonia should produce any change in the dilute solution. When ignited on platinum foil no appreciable residue should be left by 5 gr. of the salt. Commercial samples are often contaminated by potassium oxalate.

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13. AMMONIUM SULPHATE.

$(NH_4)_2SO_4$. M.W. = 132.

This salt may be prepared in the same manner as given for ammonium nitrate, using pure *dilute* sulphuric acid and pure ammonia water or ammonium carbonate (*sal volatile*). The concentrated acid must be diluted with 6 or 8 parts of water during the first part of the reaction, to prevent spattering when adding the ammonia, since the heat developed is very great.

Reaction:

$$2\ NH_4OH + H_2SO_4 = (NH_4)_2SO_4 + 2\ H_2O.$$

Properties:

Ammonium sulphate is very soluble, 100 parts of water * at

10° C.	dissolving	73.65.
20° "	"	76.30.
50° "	"	84.25.
80° "	"	92.20.
100° "	"	97.50.

The salt is insoluble in concentrated alcohol. It forms colorless crystals which melt at 140° C. and decompose at 280° C.†

* ALLUARD, Compt. Rend. **59**, 500.
† MARCHAND, Pogg. Ann. **42**, 556.

The specific gravity of the aqueous solution at 15° C. containing

10%	$(NH_4)_2SO_4$	is	1.0575.*
25%	"	"	1.1439.
35%	"	"	1.2004.
50%	"	"	1.2890.

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14. HYDROGEN-AMMONIUM-SODIUM PHOSPHATE.

(Microcosmic Salt or Salt of Phosphorus.)

$HNa{\cdot}NH_4{\cdot}PO_4{\cdot}4\ H_2O$. M.W. = 209.

Take of

Sodium phosphate (crystals),	750 gr.
Ammonium chloride (purified),	125 "
Water (boiling),	250 cc.

Into a 1500 cc. flask, put 250 cc. of water and bring to boiling. Add 750 gr. of sodium phosphate slowly, shaking well until dissolved. Heat again, and add the ammonium chloride in the same way. Shake until all is dissolved and heat to boiling, filter on a folded filter (or on a hot-water funnel, p. 13), and allow the filtrate to stand quietly to crystallize. Run the crystals through the centrifugal machine (p. 18) or drain them in a draining cone. Redissolve them in 150 cc. of boiling water, and recrystallize to free from adhering sodium chloride. Repeat the crystallization from water if necessary. Dry in the warm closet at a low temperature (30° C.), turning the crystals over frequently.

The solution of microcosmic salt should not be allowed to boil for any length of time lest a loss of ammonia should result.

* GERLACH, Zeit. anal. Chem. 8, 280.

Have the water boiling hot on adding the salt, and heat very gently, only sufficiently to dissolve it, allowing the solution to cool as quickly as possible.

Reaction:

$$HNa_2PO_4 + NH_4Cl = HNa{\cdot}NH_4{\cdot}PO_4 + NaCl.$$

Properties:

Hydrogen-sodium-ammonium phosphate forms transparent crystals with 4 molecules of water. It effloresces in dry air, and when heated loses its "water of crystallization" and fuses with decomposition to a clear glass-like mass. The heating drives off ammonia and water and leaves sodium metaphosphate ($NaPO_3$) which can combine with various metallic oxides, forming colored bodies.

The "salt of phosphorus" should fuse on a platinum wire to a colorless transparent bead. When a little copper oxide is added to the fused bead, no green nor blue coloration should be imparted to the flame. The salt dissolves in 6 parts of cold water and in 1 part of boiling water, forming a solution very slightly alkaline to litmus.

It is much used in blowpipe analysis, because of its combination with metallic oxides to form colored double phosphates; also as a means of detecting silica in minerals. When heated with alkali minerals, the salt of phosphorus bead becomes opaque.

15. ANTIMONY SULPHATE.*

$Sb_2(SO_4)_3$. M.W. = 528.

Take of

Antimony (metal),	20 gr.
Sulphuric acid, 160° Tw. (1.800 sp. gr.),	400 "

Powder the metal in a mortar, and add in small portions at a time to the boiling acid contained in a platinum or porcelain dish. Heat until the antimony is all dissolved, and allow to cool slowly. Strain the resulting crystalline mass of antimony sulphate from the acid mother liquor on a platinum cone or porcelain filter plate (p. 15), and dry on unglazed tile.

Reaction:

$$2\ Sb + 6\ H_2SO_4 = Sb_2(SO_4)_3 + 3\ SO_2 + 6\ H_2O.$$

Properties:

Antimony sulphate forms a white crystalline powder or slender needle-like crystals which readily deliquesce. It dissolves in a moderate quantity of water; when mixed with a small quantity of water the salt unites with the water to form a hard mass, and excess of cold water causes the precipitation of basic salt. When boiled with a large excess of water, the salt decomposes, forming antimony trioxide and sulphuric acid.

* ERDMANN, Präparatenkunde, I, 296.

16. ANTIMONY TRICHLORIDE.

$SbCl_3$. M.W. = 226.5.

(*a*) Take of

Antimony trioxide,	100 gr.
Hydrochloric acid, 36° Tw. (sp. gr. 1.180),	182 cc.

Put the acid into an evaporating dish, and warm slightly. Then stir in the antimony trioxide, a little at a time. When all the oxide is added, heat the dish gently, and finally bring to boiling, until any excess of hydrochloric acid is driven out and a drop of solution crystallizes when cooled on a watch glass placed on ice. Transfer the liquid to a retort with a thermometer in the tubulature and distill. The liquid first passing over is chiefly dilute hydrochloric acid, but after a time the temperature will rise to 200° C., and a drop of the distillate will solidify on a cold surface. Then collect the distillate separately as pure.

Reaction:

$$Sb_2O_3 + 6\ HCl = 2\ SbCl_3 + 3\ H_2O.$$

(*b*) Antimony trichloride may also be prepared by leading chlorine gas into an apparatus similar to that for phosphorus trichloride (p. 155), in which metallic antimony has been placed. The trichloride distills over.

Properties:

Antimony trichloride is a white or yellowish-white semisolid substance, very deliquescent. It decomposes in water but dissolves in alcohol unchanged. Its decomposition in water is prevented by the presence of a small quantity of

citric, tartaric, or hydrochloric acid. Because of its soft and buttery appearance it is called "butter of antimony." It boils at 200° C.

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17. ANTIMONY TRIOXIDE.

Sb_2O_3. M.W. = 288.

(*a*) Take of

Antimony sulphate (pulverized),	200 gr.
Water,	3000 cc.
Sodium carbonate,	125 gr.

Put 400 cc. of water into a 14-inch evaporating dish, and add the pulverized antimony sulphate cold, stirring well. Add a dilute solution of sodium carbonate (125 gr. in 2500 cc. of water), and heat to boiling. This completes the formation of the oxide. Filter off the precipitate of antimony oxide, and wash with hot water until free from sulphates. Remove excess of water by filtering on a Büchner funnel with suction (p. 14).

Reaction:

$$2\ Sb_2(SO_4)_3 + 6\ Na_2CO_3 = 2\ Sb_2O_3 + 6\ Na_2SO_4 + 6\ CO_2.$$

(*b*) Take of

Antimony sulphide,	100 gr.
Hydrochloric acid, 36° Tw. (sp. gr. 1.180),	425 cc.
Nitric acid, 68° Tw. (sp. gr. 1.34),	5 "
Water,	a sufficient quantity.

Put the mixed hydrochloric and nitric acids into a 1000 cc. flask, heat to about 50° C., and add the *finely powdered* anti-

mony sulphide in small portions at a time. When all the sulphide has been added and the evolution of hydrogen sulphide has become slow, raise the temperature very gradually until the solution comes to boiling. Boil for an hour, adding boiling water from time to time as it evaporates, keeping the contents of the flask at about 500 cc. Then transfer to an evaporating dish, and add hot water until a very slight *permanent* turbidity appears in the solution; boil for five minutes, and filter, allowing the clear filtrate to run into a large crock containing about 20 liters of cold water. A white precipitate * of a basic oxychloride of antimony falls; allow this to settle, and draw off the clear water. Boil the oxychloride several times with fresh water in portions of 2 liters each, and filter hot on the Büchner funnel (p. 14) after each boiling. This is to decompose the oxychloride into the oxide. Wash the precipitate (antimony trioxide) several times by decantation until it gives no acid reaction, and finally drain off the remaining water on a Büchner funnel with suction. Dry on a glass plate in the warm closet at a low temperature.

Properties:

Antimony trioxide is a white amorphous powder, very slightly soluble in water and very readily soluble in hydrochloric acid, but not in nitric acid. It is volatile at a red heat. It is used chiefly in the preparation of tartar emetic (p. 72).

* This precipitate is the "Algaroth powder," $Sb_4O_5Cl_2$, a basic antimony chloride ($Sb_2O_3 \cdot 2\,SbOCl$); but its composition varies somewhat according to the temperature and other conditions of its precipitation.

18. ANTIMONY-POTASSIUM TARTRATE.

(Tartar Emetic.)

$KSbO(C_4H_4O_6) + \frac{1}{2} H_2O$. M.W. = 302.

Take of

Antimony oxide,	400 gr.
Cream of tartar,	500 "
Water,	5 liters.

Put the water into a 16-inch evaporating dish, and heat to boiling. Dissolve the cream of tartar in the hot water, and add the antimony oxide slowly. When all dissolved, filter the hot solution and evaporate to crystallize.

Reaction:

$$KHC_4H_4O_6 + Sb_2O_3 = 2\ KSbO(C_4H_4O_6) + H_2O.$$

Properties:

Tartar emetic crystallizes in rhombic pyramids which are soluble in 12.6 parts of water at 21° C. The crystals effloresce somewhat when exposed to the air and when heated to 200–220° C. are partially decomposed, setting free the combined water and forming an antimony-potassium tartrate, $KSb(C_4H_2O_6)$, which again unites with water to reform ordinary tartar emetic. The salt is used extensively in dyeing and printing textile fabrics, and also as an emetic in medicine.

19. BARIUM ACETATE.

$Ba(C_2H_3O_2)_2 + H_2O$. M.W. = 273.

Take of

Witherite (powdered),	1000 gr.
Acetic acid, 8° Tw. (sp. gr. 1.040),	2000 cc.
Water,	500 "

Put the witherite into a 14-inch evaporating dish, add water to form a thick cream, add the acid in small portions at a time, stirring thoroughly, and finally heat on the steam bath until all action ceases. The solution is very syrupy and sticky, and the evolution of carbon dioxide causes the formation of a thick froth which completely fills the dish; but on standing over night this slowly disappears. Test the solution with litmus, and if found acid, add a little more witherite, or, better, some precipitated barium carbonate to make the solution neutral. Decant from the residue through a cloth filter. If too syrupy to filter well, dilute with water. Evaporate on the steam bath until crystals of barium acetate appear on the surface of the liquid, and then allow to cool. Separate the crystals from the mother liquor on the Büchner funnel (p. 14) or by the centrifugal machine (p. 18). Recrystallize from water containing a little acetic acid. Dry in a desiccator over sulphuric acid or in the drying closet at a low temperature, turning the crystals over several times. Bottle in a well-stoppered bottle as soon as dry.

Since witherite is frequently contaminated with calcium carbonate, the above process does not yield a product free from calcium acetate, but it is quite pure enough for most purposes. For a pure salt the precipitated barium carbonate prepared from nitrate as on page 74 may be used instead of witherite.

Reaction:

$$BaCO_3 + 2\ C_2H_4O_2 = Ba(C_2H_3O_2)_2 + H_2O + CO_2.$$

Properties:

Barium acetate forms white needle-like crystals containing 1 molecule of "water of crystallization." It should be pure white and free from chlorides, calcium salt, and heavy metals. It is very soluble in water forming a neutral or slightly acid solution. The salt is used as a source of barium salts which may be precipitated from it. Also as a laboratory reagent in place of the chloride or nitrate where it is not desirable to have these acids introduced into the analysis.

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20. BARIUM CARBONATE.

$BaCO_3$. M.W. = 197.

(*a*) Take of

Barium nitrate,	1000 gr.
Ammonium carbonate,	370 "
Ammonia water (sp. gr. 0.900),	300 cc.
Water,	6800 "

Dissolve the barium nitrate in 6 liters of water at 50° C., and put into a precipitation jar (Fig. IX, p. 19). Dissolve the ammonium carbonate in 800 cc. of water, and add to the nitrate solution while warm, stirring actively. When the liquid has cooled, add the concentrated ammonia until the solution has a decided odor of ammonia. This renders the barium carbonate less soluble in the ammonium nitrate solution. Allow to settle, and draw off the solution of ammonium nitrate, and transfer

the precipitate of barium carbonate to a Büchner funnel (p. 14), using the suction pump to remove as much as possible of the adhering solution. Wash several times by decantation until free from nitrate, remove excess water with the suction filter, and dry in the hot closet at 125° C.

For many purposes the carbonate need not be dried, but may be preserved wet as a thick paste.

Reaction:

$$Ba(NO_3)_2 + (NH_4)_2CO_3 = BaCO_3 + 2\ NH_4NO_3.$$

(*b*) Instead of using nitrate, the chloride or acetate of barium may be used if desired, making slight changes in the quantity of ammonium carbonate needed; or a solution of barium sulphide, made as directed in the preparation of barium chloride on page 77, may be precipitated with a carbonate solution.

(*c*) From barite:

Take of

Barium sulphate (powdered barite),	1000 gr.
Coal tar pitch,	150 "
Pearl ash (refined),	550 "

Mix the pulverized materials thoroughly, put into a Battersea crucible, and heat in the Roessler furnace to a red heat for an hour. Break out the fused mass from the crucible, and extract by boiling with water, repeating this process until all the soluble matter is removed. The residue is an impure barium carbonate which may be used in the same way as witherite as a source of barium salts (pp. 73, 76, and 80).

Properties:

Barium carbonate prepared as described in (*a*) is a heavy white powder, insoluble in water, but dissolving readily in

dilute hydrochloric or nitric acid. When precipitated by sodium or potassium carbonate from any barium salt, the product cannot be entirely freed from traces of soda or potash.

It should dissolve in dilute hydrochloric acid, forming a perfectly clear solution from which all the barium may be removed by adding sulphuric acid, while hot. The filtrate from this precipitation should not become turbid on adding alcohol and should leave only a very slight residue when evaporated to dryness. Hydrogen sulphide or ammonia with ammonium sulphide should not produce a dark-colored precipitate in the hydrochloric acid solution. No chloride should be found in the nitric acid solution nor should the acetic acid solution give any tests for nitrate.

Barium carbonate is much used in laboratory work to separate iron and aluminum from manganese, zinc, calcium, and magnesium, and to neutralize acids.

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21. BARIUM CHLORIDE.*

$BaCl_2 \cdot 2\,H_2O$. M.W. = 244.

(*a*) From witherite:

Take of

Witherite (powdered),	1000 gr.
Hydrochloric acid (sp. gr. 1.200),	710 cc.
Water,	2000 "

Mix the witherite with 1000 cc. of water in a 16-inch evaporating dish to form a paste, and add the acid previously diluted with 1000 cc. of water, in small portions at a time. The effer-

* Godin, Dingl. J. **171**, 316. Kuhlmann, Compt. Rend. **47**, 403, 464, 674.

vescence causes some frothing, and the solution should be well stirred after each addition of acid. When the action becomes slow, heat the dish on the steam bath, and make the final additions of acid to the hot solution.

Evaporate the solution to dryness on the steam bath without filtering, and heat for some time. Treat the residue and crystals of barium chloride with water, add a solution of barium sulphide — see (*b*) — until a test portion gives no precipitate with this reagent, and filter. Evaporate the filtrate after acidifying slightly with hydrochloric acid to 62° Tw. (1.312 sp. gr.), and allow to crystallize.

Witherite contains other substances besides barium carbonate, and the most troublesome of these are calcium and iron salts. By adding a small excess of finely powdered witherite to the solution after the effervescence has all ceased, and before evaporating to dryness, most of these are precipitated from the solution. The barium sulphide also precipitates the heavy metals, but traces of calcium, strontium, and the alkali metals are often found in barium chloride. By recrystallizing several times from distilled water these impurities may be removed.

Reaction :

$$BaCO_3 + 2\ HCl = BaCl_2 + CO_2 + H_2O.$$

(*b*) From barite, or precipitated barium sulphate :

Take of

Barite (powdered),	250 gr.
Charcoal (powdered) *or* Pitch,	35 "

Mix the powdered barite with the carbonaceous matter very thoroughly, and fill a G (Battersea) crucible with the mixture. Cover, and heat in the Roessler gas furnace to a bright red heat

for 1 or 2 hours. Cool, and extract the residue with hot water. Filter, and decompose the hot solution of barium sulphide by adding hydrochloric acid to it as long as hydrogen sulphide escapes on adding more acid to a test portion of the solution after boiling. When the barium sulphide is decomposed, filter, and evaporate the solution to dryness. Take up in hot water, filter if necessary, and evaporate to 62° Tw. (1.310 sp. gr.) and allow to crystallize. Free the crystals from mother liquor by the Büchner funnel and suction (p. 14). Recrystallize from distilled water.

Reactions:

$$BaSO_4 + 4\ C = BaS + 4\ CO.$$
$$BaS + 2\ HCl = BaCl_2 + H_2S.$$

Properties:

Barium chloride forms colorless crystals which dissolve in water forming a neutral solution.

100 parts of water at

0° C.	dissolve	30.9	parts	$BaCl_2$.*
10° "	"	33.3	"	"
20° "	"	35.7	"	"
30° "	"	38.2	"	"
40° "	"	40.8	"	"
50° "	"	43.6	"	"
60° "	"	46.4	"	"
72° "	"	50.0	"	"
80° "	"	52.4	"	"
90° "	"	55.6	"	"
100° "	"	58.8	"	"
104° "	"	60.2	"	"

The specific gravity of barium chloride containing

* Mulder, Scheik. Verhand. **1864**, 45.

1 %	of the salt	is	1.00917.*
5 %	"	"	1.04584.
10 %	"	"	1.09508.
15 %	"	"	1.14846.
20 %	"	"	1.20611.
25 %	"	"	1.27017.

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22. BARIUM CHROMATE.

$BaCrO_4$. M.W. = 253.5.

Take of

Barium acetate,	1000 gr.
Potassium bichromate,	540 "
Water,	3000 cc.

Dissolve the potassium bichromate in 1500 cc. of water by heating on the steam bath. Allow to settle, and decant or filter from any sediment. Transfer to a precipitation jar (p. 19), and add the barium acetate dissolved in 1500 cc. of water. A pale yellow precipitate of barium chromate falls on the addition of the acetate solution, until all the barium salt has been converted to the insoluble chromate. Allow to settle, draw off the top liquor, and fill the jar with fresh water. Continue this washing by decantation until no acetic acid or acetate can be detected in the wash waters. Drain on the cloth filter, and press in the cloth in the screw press to remove excess water (p. 18). Dry in the drying closet.

Reaction:

$$2\ Ba(C_2H_3O_2)_2 \cdot H_2O + K_2Cr_2O_7 = 2\ BaCrO_4 + 2\ KC_2H_3O_2 + 2\ C_2H_4O_2.$$

* GERLACH, Zeit. anal. Chem. 8, 283.

Properties:

Barium chromate is a pale yellow powder, insoluble in acetic acid, but dissolving in nitric or hydrochloric acid. It is used to some extent as a pigment under the name of lemon yellow. It has the advantage over chrome yellow in that it does not darken on exposure to hydrogen sulphide. But the color fades in the light and becomes greenish.

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23. BARIUM NITRATE.

$Ba(NO_3)_2$. M.W. = 261.

Take of

Witherite (powdered),	1200 gr.
Nitric acid, 50° Tw. (sp. gr. 1.250),	1540 cc.
Water,	4000 "

Put the witherite into a 16-inch evaporating dish, add 1 liter of water, and stir until thoroughly mixed. Add the acid in portions of about 100 cc. each, stirring well after each addition of acid, and waiting until the effervescence moderates before adding the next portion. When a little more than half of the acid has been added, heat the dish on the steam bath, dilute with 3 liters of hot water, and add the remainder of the acid in small portions at a time to the hot liquid, stirring thoroughly. Evaporate down to dryness on the steam bath. Treat the residue with 100 cc. of strong nitric acid, stir well, and let stand half an hour. Add 5 liters of hot water, and stir well while heating to 90° C. on the steam bath. Filter on a double cloth bag (p. 12) or by upward filtration (p. 15). Let the filtrate run into another evaporating dish, and concentrate until the formation of

a pellicle on the surface of the liquid shows it to be saturated. Wash the residue from the witherite with 1 or 2 liters of boiling water, and add these to the solution of barium nitrate. Let cool slowly, and next day pour off the supernatant liquor from the crystals. Evaporate the liquor for more crystals.

The nitrates of calcium and strontium, being more soluble than the barium salt, remain in the mother liquor. A slight excess of witherite during solution prevents the iron in the mineral from contaminating the barium nitrate.

Dissolve the combined crystal products in 5 liters of hot water, filter if necessary, add nitric acid until the solution is acid, and allow to crystallize a second time. Drain the crystals, and dry on glass plates in the drying closet at a medium temperature.

Reaction:

$$BaCO_3 + 2\,HNO_3 = Ba(NO_3)_2 + CO_2 + H_2O.$$

Properties:

Barium nitrate forms white crystals without "water of crystallization," and is not very soluble in water. 100 parts of water at

0° C.	dissolve	5.	parts	barium nitrate.*
10° "	"	7.	"	"
20° "	"	9.2	"	"
30° "	"	11.6	"	"
40° "	"	14.2	"	"
50° "	"	17.1	"	"
60° "	"	20.3	"	"
70° "	"	23.6	"	"
80° "	"	27.0	"	"
90° "	"	30.6	"	"
100° "	"	34.2	"	"

* Mulder, Scheik. Verhand. **1864**, 47.

The specific gravity of an aqueous solution at 19.5° C. containing

1%	of the	salt	is	1.009.*
2%	"	"		1.017.
3%	"	"		1.025.
4%	"	"		1.034.
5%	"	"		1.042.
6%	"	"		1.050.
7%	"	"		1.060.
8%	"	"		1.069.
9%	"	"		1.078.
10%	"	"		1.087.

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24. BISMUTH NITRATE.†

$Bi(NO_3)_3 \cdot 10\ H_2O$. M.W. = 573.5.

Take of

Metallic bismuth,	200 gr.
Nitric acid (sp. gr. 1.200),	800 cc.

Pulverize the bismuth to a coarse powder. Heat the acid in a 12-inch evaporating dish to 85° C., and add the powdered bismuth to the hot acid in *small* portions at a time, so that a steady but vigorous evolution of gas is maintained. When the metal is nearly all in solution and the action is becoming less violent, increase the heat by putting a Bunsen lamp under the dish, and finally bring to the boil for five minutes.

If arsenic is present in the bismuth, a white precipitate of bismuth arsenate may form after about one-third of the metal is dissolved. Toward the end of the reaction, when the excess

* GERLACH, Zeit. anal. Chem. **8**, 286.

† SCHNEIDER, J. pr. Chem. [2] **20**, 418. GROSSMANN, Arch. Pharm. [3] **22**, 297.

of nitric acid is nearly neutralized, a small amount of subnitrate of bismuth may also precipitate along with the arsenate. To prevent this as far as possible, an excess of nitric acid is used over the theoretical amount needed to dissolve the metal and to replace the acid lost through the violence of the reaction. The solution must be kept as concentrated as possible, however, to insure the precipitation of the arsenate and to prevent the separation of the subnitrate. The solution may be filtered on an asbestos filter (p. 12) which has previously been treated with nitric acid; or it may be allowed to stand in a covered beaker for a day or two, at a temperature of about 25° C., till the precipitate has entirely subsided; syphon off the top liquor from the residue.

Concentrate the clarified solution to about 500 cc., and allow it to crystallize. Wash the crystals in a little dilute nitric acid, and drain them or dry in the centrifugal machine. By further evaporation a second crop of crystals may be obtained, which may be impure, owing to arsenic in the mother liquor. Or the mother liquor may be poured into an equal weight of water and a precipitate of subnitrate of bismuth obtained, which, however, will not be free from arsenic.

In no case in the preparation of bismuth nitrate should water be added to the solution, and the acid used for dissolving the metal must be concentrated.

Reaction:

$$2\ Bi + 8\ HNO_3 = 2\ Bi(NO_3)_3 + 4\ H_2O + 2\ NO.$$

Properties:

Bismuth nitrate forms large colorless crystals with 10 molecules of "water of crystallization." When treated with water these decompose and form basic salts. The crystals dissolve in

dilute nitric acid. When heated to 75 ° C. they melt in their "water of crystallization."

Bismuth subnitrate is but slightly soluble in water, but dissolves in dilute nitric or hydrochloric acid. A number of basic nitrates are known, all classed under the name "subnitrate." It is used in medicine, and for such purposes should not give tests for lead, arsenic, copper, or substances insoluble in nitric acid. Neither should chlorides, sulphates, nor the alkali metals be present. By dissolving crystals of the nitrate prepared as above and then precipitating the solution with water, a pure subnitrate may be obtained.

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25. CADMIUM CHLORIDE.*

$CdCl_2 \cdot 2\ H_2O$. M.W. = 219.

Take of

Metallic cadmium,	500 gr.
Nitric acid, 48° Tw. (sp. gr. 1.240),	2000 cc.
Ammonium carbonate,	750 gr. (approx.)
Hydrochloric acid, C. P., Water,	a sufficient quantity.

"Feather" the cadmium, as described in the preparation of cadmium iodide on page 86. Put the feathered metal into a 12-inch evaporating dish, and add the nitric acid in small portions at a time. The process must be carried on under the hood because of the nitric oxide evolved. When the acid is nearly

* The process here described includes the preparation of cadmium nitrate, in solution, and of cadmium carbonate. The nitrate may be obtained crystallized by evaporating the solution.

neutralized and the action becomes quiet, heat the dish on the water bath until no more action ensues. Dilute with 1 or 2 liters of hot water, and let the dish stand quietly until all sediment has deposited.

Decant the solution into a large crock, and dilute with 20 liters of hot water. Add a concentrated solution of ammonium carbonate, a few cc. at a time, until a test portion of the liquid after filtering gives no reaction for iron. Filter off the precipitate of iron, etc., and transfer the filtrate to a precipitation jar (Fig. IX, p. 19), and add a concentrated solution of ammonium carbonate until the cadmium is all precipitated. (This requires about 750 gr. of ammonium carbonate.) Any zinc present remains in solution. Wash the precipitate (cadmium carbonate) by decantation until free from nitrates and ammonia.

Dissolve the cadmium carbonate in C. P. hydrochloric acid, taking care to use a little less acid than is necessary to dissolve the whole of the carbonate. Filter the solution, and evaporate to dryness on the steam bath. Dissolve the residue in 600 cc. of hot distilled water, add a few drops of hydrochloric acid, and allow the whole to stand for a number of hours to crystallize. Dry the crystals at a low temperature in the warm closet or in a desiccator over sulphuric acid.

Reactions:

$$3\ Cd + 8\ HNO_3 = 3\ Cd(NO_3)_2 + 4\ H_2O + 2\ NO.$$
$$Cd(NO_3)_2 + (NH_4)_2CO_3 = CdCO_3 + (NH_4)_2NO_3.$$
$$CdCO_3 + 2\ HCl = CdCl_2 + H_2O + CO_2.$$

Properties:

Cadmium chloride crystallizes with 2 molecules of "water of crystallization." The crystals effloresce when exposed to the air.

One part of the salt at

20° C.	dissolves in	0.71	parts of water.*
40° "	"	0.72	"
60° "	"	0.72	"
80° "	"	0.70	"
100° "	"	0.67	"

The specific gravity of the aqueous solution of cadmium chloride containing

13	parts of the salt	in 100	parts H_2O,	is	1.1068.
26.9	"	"	"	"	1.2106.
41	"	"	"	"	1.3100.
55.8	"	"	"	"	1.4060.
72.5	"	"	"	"	1.5060.
114.2	"	"	"	"	1.7266.

It is also soluble in alcohol. The anhydrous salt melts at 540° C. and volatilizes undecomposed at higher temperatures.

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26. CADMIUM IODIDE.

CdI_2. M.W. = 366.

Take of

Cadmium (metal),	150 gr.
Iodine,	340 "
Water,	1000 cc.

"Feather" the cadmium by melting it and pouring the liquid metal from a height of 3 or 4 feet into water contained in a 4-gallon crock. Weigh out 150 gr. of the dry feathered metal, and put it into a wide-mouthed bottle of 1500-cc. capacity, containing 1000 cc. of water and 340 gr. of iodine. Cover the bottle mouth with a watch glass, and allow it to stand quietly

* KREMERS, Pogg. Ann. **103**, 57.

in a large pan of water on the steam table where the temperature will range from 75–85° C. Stir the contents of the bottle occasionally with a glass rod. After 3 or 4 days the metal will be mostly dissolved. Pour into a 12-inch evaporating dish, heat to boiling for 20 minutes, filter hot, evaporate the solution until saturated, and allow to crystallize. Drain the crystals, and dry in a desiccator over sulphuric acid. Concentrate the mother liquor further for more crystals.

Reaction:

$$Cd + I_2 = CdI_2.$$

Properties:

Cadmium iodide crystallizes in thin white plates, soluble in water, alcohol, and ether.

One part of the salt at

15° C.	dissolves	in	1.3	parts	of water.*
20°	"	"	1.08	"	"
40°	"	"	1.00	"	"
60°	"	"	0.93	"	"
80°	"	"	0.86	"	"
100°	"	"	0.75	"	"

The specific gravity of $CdI_2 + aq$ at 19.5° C. containing

5%	CdI_2	is	1.044.†
10%	"		1.088.
15%	"		1.138.
20%	"		1.194.
25%	"		1.253.
30%	"		1.319.
35%	"		1.395.
40%	"		1.476.
45%	"		1.575.
50%	"		1.680.

This salt finds a limited use in photography but is of little commercial importance.

* Kremers, Pogg. Ann. **103**, 57.

† Gerlach, Zeit. anal. Chem. **8**, 285.

27. CALCIUM CARBONATE.

$CaCO_3$. M.W. = 100.

Prepare a solution of calcium chloride free from iron, magnesia, etc., as directed on page 90; or take the solution obtained from a Kipp's apparatus which has been used for generating carbon dioxide. After having purified and filtered the solution, heat it to 90° C., and add a concentrated solution of commercial ammonium carbonate in water, together with a little ammonia water, until a test filtered off gives no precipitate with these reagents. Allow it to settle, and decant the liquid through a Büchner suction filter (p. 14), finally bringing the precipitate into the filter. Wash with hot water until the wash water is free from chlorides. Dry the precipitate on a glass plate in the hot closet, and finally heat to 125° C. for a couple of hours and bottle the pure white powder.

Properties:

Calcium carbonate is entirely soluble in hydrochloric acid, yielding a clear solution which should not be altered by barium chloride, ammonia, sodium phosphate, nor ammonium molybdate, *i.e.*, it should contain no sulphates, iron, alumina, magnesia, nor phosphoric acid. It is useful as a standardizing material in acidimetry. When ignited at a red heat for some time carbon dioxide escapes and calcium oxide remains.

28. CALCIUM CHLORIDE (Porous).

$CaCl_2$. M.W. = 111.

Take of

Quicklime,	500 gr.
Hydrochloric acid (sp. gr. 1.200),	1640 cc.

Slake the lime, and stir up to a thin milk with water. After decanting the "milk" from the coarse insoluble impurities (see DECANTATION, p. 19), put 100 cc. of it into a porcelain dish, and slowly add hydrochloric acid until the solution is acidified. Add another 100 cc. of the milk, and neutralize with acid, continuing until all the acid is neutralized and the solution made slightly alkaline by a small excess of lime. Boil for a few minutes. Decant the settled clear liquid from the sediment as far as possible, and filter the remainder with suction. (See FILTRATION, p. 13.) Evaporate the filtrate over the lamp until nearly all the water is gone and the liquid is so thick that test portions solidify on cooling. Then add 50 cc. of hydrochloric acid, which causes the mass to swell. Allow it to cool and set with only occasional stirring. Dry by heating in a bright iron pan over the lamp, but do not let it become hot enough to fuse the calcium chloride. The yield should be about 1 kg.

The solution of calcium chloride obtained by generating carbon dioxide from marble and hydrochloric acid, as in a Kipp's apparatus, is a favorable source for this preparation. It must usually be neutralized with a small amount of "milk of lime" to precipitate iron, etc., before evaporating the solution to obtain the calcium chloride.

Properties:

This substance should be nearly white and perfectly dry. If much iron or other impurity is present the color varies, but is more or less gray or brown. Its chief use is to absorb moisture from gases or to remove traces of water from organic liquids in which calcium chloride itself is insoluble. It is also much used as a drying agent in desiccators.

100 parts of water at

0° C.	dissolve	49.6	parts $CaCl_2$.*
10° "	"	60.	"
15° "	"	66.	"
20° "	"	74.	"
25° "	"	82.	"
30° "	"	93.	"
33° "	"	100.	"
40° "	"	110.	"
50° "	"	120.	"
60° "	"	129.	"
70° "	"	136.	"
80° "	"	142.	"
90° "	"	147.	"
94° "	"	150.	"
99° "	"	154.	"
179.5° "	"	325.	"

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29. CALCIUM CHLORIDE (Crystals).

$CaCl_2 \cdot 6\,H_2O$. M.W. = 219.

Make a solution of calcium chloride by neutralizing hydrochloric acid with quicklime (p. 89) or marble. Use a slight excess of lime. Add 25 cc. of chlorine water to each 2 liters of the solution, and boil half an hour. Then add a few cc. of "milk of lime" to the solution until strongly alkaline, and

* MULDER, Scheik. Verhand. **1864**, 107.

boil again until a filtered test portion gives no blue color with potassium ferrocyanide and hydrochloric acid. Filter boiling hot, by which the precipitation of any calcium sulphate is rendered more complete. Evaporate the filtrate in a porcelain dish over the lamp to a density of 75° Tw. (sp. gr. 1.375), and allow it to cool slowly. Or the concentrated solution may be put in the hot closet at 60° C. and the growth of the crystals watched from day to day until the desired size is obtained. They should be rapidly freed from adhering mother liquor, by draining in a *covered* funnel or by wiping with scraps of filter paper, and dried in a desiccator over sulphuric acid and bottled at once in a dry and cold bottle which is tightly stoppered.

Fresenius recommends passing hydrogen sulphide into the solution containing some slaked lime, until a filtered test portion shows no change with ammonium sulphide. Then digest at a gentle heat for 12 hours in a covered vessel. Filter and crystallize as above.

Properties:

Crystallized calcium chloride is a very deliquescent substance and melts in its 6 molecules of "water of crystallization" if warmed to 28 or 30° C. When dissolved in water much heat is aborbed, and when mixed (3 parts) with snow (2 parts) a temperature of —35 to —40° C. is attained. It is entirely soluble in 10 parts of absolute alcohol.

Calcium chloride should dissolve in water to form a clear solution, without leaving any residue. The aqueous solution is neutral, and when heated with caustic soda or potash must not liberate ammonia. Hydrogen sulphide should cause no precipitation nor change of color in the solution. It finds use as a qualitative reagent in the separation of certain organic acids.

30. CHLOROPLATINIC ACID.

(Platinum Chloride.)

$H_2PtCl_6 \cdot 6\ H_2O$. M.W. = 517.

(*a*) From scrap platinum: *

Dissolve scrap platinum in *aqua regia* (5 HCl to 1 HNO_3), and evaporate the solution to dryness. Dissolve in moderately strong hydrochloric acid, and evaporate to dryness again. Dissolve in hot water, adding a few cc. of strong hydrochloric acid while dissolving. Add a considerable excess of sodium hydrate solution, and boil for an hour, adding a few drops of alcohol once or twice during the boiling to destroy any sodium hypochlorite in the solution. Redissolve the precipitate in hydrochloric acid, filter if not clear, and add a hot saturated solution of ammonium chloride as long as a precipitate falls. Separate the yellow precipitate of ammonium chloroplatinate, $(NH_4)_2PtCl_6$, by decantation and wash with *cold*, very dilute hydrochloric acid, and dry on a glass plate. Heat in a porcelain crucible over the lamp until all ammonia and chlorine are driven off; or ignite in a glass combustion tube in a stream of dry coal gas or hydrogen.

Weigh the reduced platinum and dissolve in *aqua regia* (5 HCl to 1 HNO_3), and evaporate to dryness on the steam bath, adding hydrochloric acid at intervals during evaporation to expel all traces of nitric acid. Redissolve the residue in dilute hydrochloric acid, and evaporate down on the steam bath to crystallize.

The purpose of boiling with caustic soda is to reduce any iridium tetrachloride formed by the *aqua regia*, to the trichloride, which forms a soluble double salt with ammonium chloride. The platinum tetrachloride is not reduced by the caustic soda.

* After THORPE, Quantitative Chem. Analysis, 7th ed., 381.

(*b*) From laboratory residues :

Boil the residues of platinum salts with a solution of sodium carbonate, and add some alcohol during the boiling. Decant the liquid from the platinum which is precipitated as a black powder. Wash the platinum precipitate several times with boiling water by decantation and then with hot hydrochloric acid. Dry and weigh the platinum and dissolve in the required amount of *aqua regia* (5 HCl to 1 HNO_3), and evaporate the filtered solution on the steam bath to crystallize, adding hydrochloric acid from time to time during the evaporation to drive off all traces of nitric acid.

Properties :

Chloroplatinic acid is formed by the combination of platinum tetrachloride with hydrochloric acid. It crystallizes with 6 H_2O and is deliquescent in the air. It is entirely soluble in alcohol, leaving no residue when pure. The ammonium and potassium salts are very difficultly soluble in water, while the sodium chloroplatinate is readily soluble. On this fact depends its use as a laboratory reagent in the separation of potassium and sodium.

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31. CHROMIUM ACETATE.

$Cr(C_2H_3O_2)_3$ or $Cr_2(C_2H_3O_2)_6$. M.W. = 229.5.

Take of

Chrome alum,	1000 gr.
Soda ash (58% Na_2O),	330 "
Acetic acid (30%),	1200 cc.
Water,	4750 "

Dissolve the chrome alum in a 16-inch evaporating dish with 4 liters of water at 40° C., and add the solution of soda ash dis-

solved in 750 cc. of water at 32° C., taking care to add but little at a time and to stir well after each addition. Filter off the green precipitate of chromium hydrate, wash with warm water by decantation, and finally press in a cloth bag (p. 18) to remove as much water as possible. Break up the cake of hydrate, and, while still damp, dissolve it in the acetic acid by warming and stirring. Evaporate the solution to dryness on the steam bath, or stop the evaporation when the density reaches 32° Tw. (sp. gr. 1.160).

Reactions:

$$2\ KCr(SO_4)_2 \cdot 12\ H_2O + 3\ Na_2CO_3 = K_2SO_4 + 3\ Na_2SO_4 + 3\ CO_2 + 2\ Cr(OH)_3 + 21\ H_2O.$$

$$Cr(OH)_3 + 3\ C_2H_4O_2 = Cr(C_2H_3O_2)_3 + 3\ H_2O.$$

Properties:

Chromium acetate is usually sold in commerce as a solution at 32° Tw., as it does not crystallize well. However, crystals having the composition $Cr(C_2H_3O_2)_3 + H_2O$ have been isolated. Many basic chromium acetates are known.

If made below 60° C. the solution is violet, but becomes greenish on heating. Chromium acetate is very soluble in water. The aqueous solution is not easily precipitated cold by alkaline hydrates, carbonates, nor phosphates, but the precipitation takes place on boiling. It finds some use as a mordant in calico printing.

32. CHROMIUM HYDRATE.

$Cr(OH)_3$ or $Cr_2(OH)_6$. M.W. = 103.5.

(*a*) Take of

Chromium sulphate,	200 gr.
Ammonia (sp. gr. 0.958),	290 cc.
Water,	200 "

Dissolve the sulphate in the water, and add the ammonia to the solution at 50° C., stirring actively. Then bring to boiling for 20 minutes. A green precipitate of chromium hydrate falls; it is best to allow this to settle and to draw off or decant the top liquor containing ammonium sulphate. Wash the precipitate by decantation until free from sulphate. Drain in a cloth bag filter (p. 10). Dry in the warm closet, and pulverize in a mortar.

Reaction:

$$Cr_2(SO_4)_3 + 6\ (NH_3 + H_2O) = 2\ Cr(OH)_3 + 3\ (NH_4)_2SO_4.$$

Caustic soda or potash may be used instead of ammonia if desired, but the resulting sulphate of sodium or potassium is very difficult to remove completely from the precipitate of chromium hydrate.

(*b*) Take of

Potassium bichromate,	100 gr.
Water,	1200 cc.

Dissolve the bichromate in the water, put the solution into a flask or covered beaker, and pass into it a strong stream of hydrogen sulphide until the precipitate, which is brown at first,

becomes uniformly pale green in color. Filter on a cloth in a Büchner funnel (p. 14), transfer the precipitate of chromium hydrate to a dish or precipitation jar (Fig. IX, p. 19), and wash with water by decantation till the wash waters give no hydrogen sulphide test when acidified with hydrochloric acid. Free the chromium hydrate from water by use of the filter pump and Büchner funnel, and dry, if so desired, at a low temperature. As thus prepared the hydrate contains considerable free sulphur.

Reaction:

$$K_2Cr_2O_7 + 5\ H_2S = 2\ Cr(OH)_3 + 2\ KHS + H_2O + 3\ S.$$

This hydrate may be dissolved in acids to form chromium salts; the free sulphur remains undissolved and can be easily filtered off.

Properties:

Chromium hydrate forms a green powder, insoluble in water, its color varying according to the method of preparing it. If dried above 100° C. its color changes to dirty black, but it does not give up its water of hydration until heated to 200° C. or more. Then it passes over to green chromic oxide. Chromium hydrate dissolves in caustic soda or potash, forming salts of the alkali metal, called "chromites"; but these are unstable bodies, known only in solution

$$Cr(OH)_3 + 3\ NaOH = Cr(ONa)_3 + 3\ H_2O.$$

When boiled for some time the chromite solution is decomposed and chromium hydrate is reprecipitated. The chromites are also decomposed, even by weak acids and by ammonium salts.

33. CHROMIUM HYDRATE.

(Guignet's Green.*)

$Cr_2O(OH)_4$.

Take of

Potassium bichromate,	100 gr.
Boric acid (crystals),	300 "
Water to make a paste.	

Mix these materials thoroughly in a Battersea G crucible, and heat in the Roessler furnace, but not above red heat. Oxygen and water escape, and the mass swells. Allow to cool; break out the fused substance from the crucible, and boil with water to remove boric acid. A chromium borate is formed in the fusion, which decomposes when treated with water, forming the chromium hydrate as above. To remove the last traces of boric acid, boil with dilute caustic soda solution, and wash again with hot water.

Properties:

The chromium hydroxide obtained by this process is insoluble in water and cold acids, but is slowly decomposed by boiling acid. It is used as a fine green pigment in paints and for calico printing.

* GUIGNET, Bull. Soc. Chim. **1** (**1859**), 9.

34. CHROMIUM SULPHATE.

$Cr_2(SO_4)_3 \cdot 15\ H_2O$. M.W. = 663.

Take of

Chromium hydroxide (dry),	800 gr.
Sulphuric acid, 140° Tw. (sp. gr. 1.700),	850 cc.

Put the acid into a 14-inch evaporating dish, and heat to 40° C. Add the hydroxide in small portions at a time, stirring well after each addition. If the temperature is not allowed to go above 60° C., a violet-colored solution of chromium sulphate is formed. If the solution is heated to near the boiling point, the color changes to green and no crystals will deposit until, after long standing, the green solution changes over to the violet modification. The addition of dilute alcohol to the solution hastens crystallization.

Reaction:

$$2\ Cr(OH)_3 + 3\ H_2SO_4 = Cr_2(SO_4)_3 + 6\ H_2O.$$

Properties:

Chromium sulphate is soluble in 0.833 parts of water at 20° C. When heated the solution becomes green, the change taking place at about 65° C. The addition of nitric or sulphuric acid also causes this change. The green aqueous solution changes to the violet modification on standing several weeks.

The specific gravity of an aqueous solution of the violet modification containing

5%	of the salt	is	1.0275.*
10%	"	"	1.0560.
20%	"	"	1.1150.
30%	"	"	1.1785.
40%	"	"	1.2480.
50%	"	"	1.3250.

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35. CHROMIUM TRIOXIDE.†

(Chromic Anhydride.)

CrO_3. M.W. = 100.5.

Take of

Potassium bichromate,	1000 gr.
Sulphuric acid,	1850 cc.
Nitric acid, 92° Tw. (sp. gr. 1.460),	225 "
Water,	1600 "

Dissolve the bichromate in 1600 cc. of hot water in a 14-inch evaporating dish, and add 1350 cc. of concentrated sulphuric acid very cautiously, while stirring actively. Then let it stand over night in a cool place, and next day decant the solution from the crystals of potassium sulphate that have deposited. Heat the solution to 90° C., and add 500 cc. more of the concentrated sulphuric acid; if a precipitate of chromic anhydride separates, add water until this just dissolves. Evaporate until the trioxide begins to form crystals in the liquid, and then let it stand for a day or two in a cool place. Decant the mother

* GERLACH, Zeit. anal. Chem. **28**, 494.

† After ZETNOW, Pogg. Ann. **143**, 468.

liquor from the crystals of chromic anhydride, and evaporate further for more crystals. Drain and wash with 150 cc. of very concentrated nitric acid (92° Tw., sp. gr. 1.460); drain and wash again with 75 cc. of the concentrated acid. This removes adhering sulphates and sulphuric acid. Concentrated nitric acid must be used because dilute acid will dissolve the crystals. Finally dry the crystals in a small evaporating dish on the sand bath or in the drying closet.

Reaction:

$$K_2Cr_2O_7 + H_2SO_4 = 2\,CrO_3 + K_2SO_4 + H_2O.$$

Properties:

Chromium trioxide forms needle-like deliquescent crystals of a deep red color. It is very soluble in water, forming a solution of chromic acid. It is a powerful oxidizing agent, the reaction on organic matter being so violent in many cases that fire ensues.

The specific gravity of the aqueous solution at 15° C. containing

5%	CrO_3 is	1.037.*
10%	"	1.076.
15%	"	1.118.
20%	"	1.162.
25%	"	1.208.
30%	"	1.258.
35%	"	1.312.
40%	"	1.373.
45%	"	1.440.
50%	"	1.512.
55%	"	1.587.
60%	"	1.665.

Chromium trioxide as such is not very extensively used in the arts, a mixture of potassium bichromate and sulphuric acid

* GERLACH, Zeit. anal. Chem. **27**, 300.

being employed instead. It is used somewhat in organic preparation work and analyses. Commercial samples are frequently contaminated with sulphates and free sulphuric acid.

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36. CUPRIC CHLORIDE.

$CuCl_2 \cdot 2\ H_2O$. M.W. = 170.5.

(*a*) Take of

Copper sulphate (crystallized),	3000 gr.	
Soda ash,	1400 "	(approx.)
Hydrochloric acid, 36° Tw. (sp. gr. 1.180),	2150 cc.	(approx.)
Water,	6000 "	

Dissolve the copper sulphate (bluestone) in 6 liters of hot water in a 4 or 6 gallon earthenware crock, using a steam coil of copper pipe to heat the liquid. When the copper sulphate is all dissolved, add a concentrated solution of soda ash in warm water to the copper solution, a few cc. at a time, until carbon dioxide ceases to be given off. Keep the solution hot by means of the steam coil during the precipitation. Much care is necessary to prevent frothing over the top, owing to the vigorous effervescence. When the action ceases, fill the crock with water, stir well, and let it stand quietly until the basic copper carbonate * settles. Syphon off the top liquor, which may be concentrated to recover the sodium sulphate (p. 203) if desired.

* This has the probable composition $CuCO_3$, $Cu(OH)_2 + H_2O$, but this is not certain, as it varies somewhat according to the conditions of the precipitation. It is of a bluish green color and is rather difficult to filter. It holds persistently to traces of the alkali sulphate and can scarcely be freed from this impurity by long washing. But it is a most convenient material for the preparation of other copper salts, and yields products quite pure enough for most purposes.

Wash the green precipitate of basic copper carbonate with water until the wash waters are free from sulphates. Filter, and press the precipitate (p. 18) to remove the surplus water, and dissolve the mass in hydrochloric acid (sp. gr. 1.200), adding a few cc. at a time until the copper carbonate is nearly all dissolved. Heat on the steam table about an hour, and filter hot on glass wool or asbestos (p. 15). Concentrate the green filtrate of copper chloride to a density of 88° Tw. (sp. gr. 1.442), and allow it to stand quietly to crystallize. Drain the needle-like crystals in a Büchner funnel by the aid of suction (p. 14), and dry them at a low temperature in the warm closet (p. 25). Bottle at once in a *dry* bottle, and stopper tightly. Evaporate the mother liquor down to small bulk for more crystals.

Reactions:

$$2\ CuSO_4{\cdot}5\ H_2O + 2\ Na_2CO_3 = 2\ Na_2SO_4 + CuCO_3{\cdot}Cu(OH)_2 + CO_2 + 9\ H_2O.$$

$$CuCO_3{\cdot}Cu(OH)_2 + 4\ HCl = 2\ CuCl_2 + 3\ H_2O + CO_2.$$

(*b*) Take of

Copper oxide (copper scales),	280 gr.
Hydrochloric acid, 36° Tw. (sp. gr. 1.180),	640 cc.
Nitric acid, 67° Tw. (sp. gr. 1.335),	50 "

Put the copper scales into a 12-inch evaporating dish, and add just enough water to make a thick paste. Add the hydrochloric acid slowly, stirring constantly, and allow the reaction to continue as long as it will without heating. Then heat the solution nearly to boiling, and stir well at frequent intervals. Add the nitric acid to the hot liquid, a very few cc. at a time, stirring thoroughly after each addition. This oxidizes any cuprous chloride to the cupric state. A very active effer-

vescence occurs, and great care must be exercised in adding the nitric acid lest the solution boil over. When the action ceases, boil to drive off any undecomposed nitric acid. Test the solution for cuprous chloride by allowing one drop of the liquid to fall into a test tube full of cold water. If any cuprous salt is present a white turbidity will appear in the water. If only cupric salt is present the water takes on a very faint greenish tinge. Filter on an asbestos filter, using the suction pump (p. 13). Evaporate the green filtrate of cupric chloride until it reaches a density of 88° Tw., and put into a cool place to crystallize. [J. W. SMITH, private communication.]

Since copper scales contain more or less cuprous oxide and sometimes small quantities of metallic copper, no exact equation can be shown; neither are the amounts of acids given above more than approximate.

Properties:

Cupric chloride forms slender deliquescent crystals of pale green color. The salt is very soluble, 100 parts of water at 16° C. dissolving about 120 parts of the crystallized salt.*

The specific gravity of the aqueous solution at 17.5° C. containing

5%	of the salt	is	1.0455.†
10%	"	"	1.0920.
15%	"	"	1.1565.
20%	"	"	1.2223.
25%	"	"	1.2918.
30%	"	"	1.3618.
35%	"	"	1.4447.
40%	"	"	1.5284.

When heated in a porcelain dish on the steam bath and then gently over the lamp, the "water of crystallization" is driven off and a brown anhydrous powder remains, which dissolves

* RÜDORFF, Ber. **6**, 484.

† FRANZ, J. pr. Chem. [2] **5**, 274.

readily in water to form a green solution of cupric chloride. Solutions of copper chloride dissolve cellulose and should not be filtered on paper or cotton cloth.

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37. CUPRIC-AMMONIUM CHLORIDE.

$CuCl_2 \cdot 2\ NH_4Cl \cdot 2\ H_2O$. M.W. = 277.5.

Cupric-Potassium Chloride.

$CuCl_2 \cdot 2\ KCl \cdot 2\ H_2O$. M.W. = 319.5.

To make the cupric-ammonium chloride:

Take of

Cupric chloride (crystallized),	340 gr.
Ammonium chloride (purified),	214 "
Water,	1850 cc.

Dissolve the cupric chloride and the ammonium chloride separately, each in 925 cc. of hot water, and mix the two solutions, stirring thoroughly. Evaporate on the steam bath to a density of 55° Tw. (sp. gr. 1.275) and allow to crystallize. Decant the mother liquor and drain the crystals, drying them in the warm closet at a temperature of about 25° C. for 24 hours, and finally, at about 50° C., for another day. Evaporate the mother liquor further for more crystals, adding a few cc. of ammonia to replace what may have been lost in evaporating. Recrystallize these crystals from water, and dry as above.

Properties:

Cupric-ammonium chloride forms bluish green crystals which are soluble in 2 parts of water and also in alcohol. A concentrated aqueous solution of the salt is used in the determination

of carbon in iron and steel, as it dissolves the iron without forming any volatile compounds of carbon.

Cupric-potassium chloride is made in the same general way as the above, substituting potassium chloride for the ammonium chloride, and evaporating the solution of the double salt down to 90° Tw. (sp. gr. 1.450) before allowing to crystallize. The crystals are bluish green, very similar to the ammonium salt, and are used for the same purpose in iron and steel analysis.

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38. CUPRIC SULPHATE.

(Blue Vitriol.)

$CuSO_4 \cdot 5\ H_2O$. M.W. = 249.4.

(*a*) Very pure crystallized copper sulphate may be obtained by evaporating the solution left in the flask after the preparation of sulphur dioxide (p. 220). The solution should be diluted and filtered before evaporating to the crystallizing point.

(*b*) Commercial copper sulphate or "bluestone" contains some iron. This may be removed as follows:

Dissolve 2 kg. of bluestone in 2 liters of hot water and bring to boiling. Add about 25 gr. of lead peroxide, and boil the mixture for an hour, replacing the water lost by evaporation. Then take out a test portion of 10 cc. of the solution, cool, and add a few cc. of barium carbonate paste and shake for ten minutes. Warm slightly, and filter into another test tube. Add ammonia to the filtrate until the green copper hydrate precipitated at first just redissolves. Pour the ammoniacal solution into a fresh filter, and, after it has run through, wash the filter with water once or twice to remove the blue coloration. If this washing discovers a red or brown precipitate on the filter, the iron has not been completely oxidized by boiling

with the lead peroxide. In this case, again add 10 gr. of lead peroxide to the solution of bluestone, boil another half hour, and repeat the test for iron.

If no red nor brown coloration is seen on the filter paper, dilute the solution of cupric sulphate, and let it cool. Then add 25 cc. of barium carbonate paste (p. 75) and stir well while cold. Let it stand several hours, stirring frequently, and then warm * and filter. The precipitate is very fine, and it is difficult to remove it all at one filtration. Evaporate the solution to 51° Tw. (sp. gr. 1.256), and filter again if turbid in the slightest degree. Let it cool slowly, and large blue crystals of copper sulphate separate. Fine crystals may be obtained if the solution is stirred as it cools. Evaporate the mother liquor for more crystals. Drain them in a funnel, and spread on a plate in the coolest part of the warm closet for a short time to dry. If left here too long, efflorescence is very apt to take place.

Properties:

Solubility in 100 parts of water.

Temperature.	$CuSO_4 \cdot 5H_2O$.†	$CuSO_4$.‡	
0° C.	———	15.5	
10° "	36.95	19.0	
15° "	———	20.5	
20° "	42.31	22.0	
25° "	———	23.7	
30° "	48.81	25.5	
40° "	56.90	29.5	
50° "	65.83	33.6	
60° "	77.39	39.0	
70° "	94.60	45.7	
80° "	118.03	53.5	
90° "	156.44	62.7	
100° "	203.32	73.5	
104° "	———	77.95	

* By warming the mixture, the barium carbonate may also precipitate any zinc or nickel present in the solution.

† Poggiale, Ann. Chim. Phys. [3] **8**, 463.

‡ Mulder, Scheik. Verhand. **1864**, 79.

The specific gravity of the aqueous solution at 18° C. containing

1%	$CuSO_4 \cdot 5\ H_2O$	is	1.0063.*
5%	"	"	1.0319.
10%	"	"	1.0649.
15%	"	"	1.0993.
20%	"	"	1.1354.
25%	"	"	1.1738.
30%	"	"	1.2146.

Copper sulphate forms triclinic crystals of a dark blue color. When heated to 200° C., all the "water of crystallization" is expelled and a white powder is left which is exceedingly hygroscopic.

Calcined copper sulphate is often used to abstract water from alcohol and other liquids in which it is insoluble. Crystallized copper sulphate is used to some extent in dyeing, as a preservative agent, as the source of other copper salts, etc.

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39. FERRIC CHLORIDE.

$FeCl_3 \cdot 6\ H_2O$ or $Fe_2Cl_6 \cdot 12\ H_2O$. M.W. = 270.5.

(*a*)† Take of

Iron (nails or bands),	75 gr.
Hydrochloric acid, 36° Tw. (sp. gr. 1.180),	345 cc.
Nitric acid, 68° Tw. (sp. gr. 1.340),	30 "
Water,	150 "

Put the iron into a liter flask with 227 cc. of the hydrochloric acid which has been diluted with 125 cc. of water. The solu-

* Schiff, Gerlach, Zeit. anal. Chem. **8**, 288.

† After U. S. Pharmacopoeia, **1890**.

tion of the iron is slow at first but soon becomes very active, and the liquid becomes pale green in color. Cover the mouth of the flask with a watch glass, and let it stand on the steam table until all action ceases. A solution of ferrous chloride is thus obtained. Heat to boiling, and filter hot through a folded filter, into another flask containing 119 cc. of the hydrochloric acid. Wash the residue and the flask once with a very little hot water, pouring the wash water through the filter. Weigh a 10-inch evaporating dish, then put into it 30 cc. of nitric acid, and add the mixture of ferrous chloride and hydrochloric acid in a slow fine stream. A vigorous effervescence takes place, and the green color changes to brown. When effervescence ceases, heat the dish on a sand bath until all the nitric acid has been expelled. Dilute a few drops of the solution with water, and test with ferricyanide of potassium solution. If a blue color or precipitate forms, add nitric acid drop by drop until no more ferrous salt remains. Evaporate the liquid down somewhat, and add 22 cc. of hydrochloric acid. Dilute if necessary with sufficient water to make the total contents of the dish weigh 300 gr., and put it under a bell jar in a cool place for some days. The entire solution gradually solidifies into a single cake of ferric chloride. Break this into lumps, put into a dry, cold bottle, and keep in a cool place, protected from light.

Reactions:

$$Fe + 2\,HCl = FeCl_2 + H_2.$$

$$2\,FeCl_2 + 2\,HCl + O = 2\,FeCl_3 + H_2O.$$

(*b*) Take of

Metallic iron (nails or bands),	75 gr.
Hydrochloric acid, 36° Tw. (sp. gr. 1.18),	225 cc.
Water,	150 "

Put the iron into a liter flask, add the acid diluted with the water, and allow it to stand until all action ceases. Then conduct a stream of chlorine gas (p. 40) into this solution of ferrous chloride until a drop or two of the liquid diluted with 5 cc. of water gives no blue nor green color, but becomes brown with potassium ferricyanide solution. Evaporate down to a thick liquid, by which all excess of chlorine is driven off, and allow it to stand quietly for some days to crystallize. If the solution be concentrated to 1.5 sp. gr. and then cooled down to 10° C., crystals having the composition $Fe_2Cl_6 \cdot 6\,H_2O$ separate.*

(*c*) Ferric chloride may also be prepared by dissolving the ferric hydrate from experiments on pages 163, 173 in hydrochloric acid.

Properties:

Ferric chloride, frequently called "sesquichloride of iron," is a yellow crystalline mass, very soluble in water and deliquescent in damp air. It melts in its water of crystallization at 35° C. On heating strongly, water and hydrochloric acid escape, and some anhydrous salt volatilizes, leaving a residue of ferric oxide. The aqueous solution is of a dark reddish brown color, and is thick and oily in appearance. The salt is also soluble in alcohol and ether.

The specific gravity of aqueous solution of ferric chloride at 17.5° C. containing

10%	of the	salt is	1.0734.†
20%	"	"	1.1542.
30%	"	"	1.2568.
40%	"	"	1.3622.
50%	"	"	1.4867.
60%	"	"	1.6317.

* WITTSTEIN, Repertor. d. Chem. [2] **36**, 30.

† FRANZ, J. pr. Chem. [2] **5**, 283.

Ferric chloride finds some use as a laboratory reagent, in medicine and as a disinfectant. The usual impurities present are arsenic, copper, and nitric acid.

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40. FERRIC HYDRATE.*

(Ferric Hydroxide.)

$Fe_2O_3 \cdot x\,H_2O$ or $Fe(OH)_3$. M.W. = 107.

Take of

Ferric sulphate solution (p. 112),	200 cc.
Ammonia hydrate (sp. gr. 0.960),	225 "
Water,	2500 "

Dilute the ammonia with 500 cc. of water, and put the solution into a precipitation jar (Fig. IX, p. 19). Dilute the ferric sulphate with 2000 cc. of water, and add to the dilute ammonia, stirring actively. Let the jar stand quietly until the red precipitate of ferric hydrate settles, and draw off the clear liquid, which may be evaporated for the recovery of ammonium sulphate if desired. Wash the ferric hydrate with cold water until the wash waters show no more than a trace of sulphate. Put the wet precipitate on a cloth filter (p. 10), and let it drain. Then fold in the cloth, and press in the screw press, or put into a Büchner funnel and remove excess water by suction (p. 13). Dry on glass plates in the warm closet.

Reaction:

$$Fe_2(SO_4)_3 + 6\,NH_4OH = 2\,Fe(OH)_3 + 3\,(NH_4)_2SO_4.$$

* After the U. S. Pharmacopoeia, 1890.

Properties:

Ferric hydrate is a red powder, insoluble in water but soluble without residue in hydrochloric and sulphuric acids, forming ferric salts. When heated, the hydroxide loses water and passes over to the oxide.

When moist and freshly precipitated it is used as an antidote for arsenical poisoning. Its composition varies much according to the method of its preparation.

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41. FERRIC NITRATE.

$Fe(NO_3)_3$.	M.W. = 242.
$Fe(NO_3)_3 \cdot 6\,H_2O$.	M.W. = 350.
$Fe(NO_3)_3 \cdot 9\,H_2O$.	M.W. = 410.

Take of

Iron (bands or nails, bright),	100 gr.
Nitric acid, 67° Tw. (sp. gr. 1.335),	630 cc.

Put the acid into a 10-inch evaporating dish and warm to 60–70° C. Add the iron a few bits at a time, and allow the action to proceed until a red brown precipitate of basic ferric nitrate begins to form. Filter the red brown solution on glass wool (p. 12) or decant it, add an equal bulk of very concentrated nitric acid (sp. gr. 1.420), and allow to stand in a cool place to crystallize. Colorless crystals of the nitrate finally separate, which contain 6 or 9 H_2O, according to the concentration of the solution. Pour off the acid mother liquor and dry the crystals in a desiccator over sulphuric acid.

Reaction:

$$Fe + 4\,HNO_3 = Fe(NO_3)_3 + 2\,H_2O + NO.$$

Properties:

Ferric nitrate forms colorless crystals which are deliquescent in the air. They are very soluble in water and also dissolve in alcohol.

The specific gravity of a solution of ferric nitrate at 17.5° C. containing

5%	of the	salt	is	1.0398.*
10%	"	"		1.0770.
15%	"	"		1.1182.
20%	"	"		1.1612.
25%	"	"		1.2110.
30%	"	"		1.2622.
35%	"	"		1.3164.
40%	"	"		1.3746.
45%	"	"		1.4338.
50%	"	"		1.4972.
55%	"	"		1.5722.
60%	"	"		1.6572.
65%	"	"		1.7532.

The solution obtained by dissolving the iron is used for dyeing black on silk and buff on cotton.

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42. FERRIC SULPHATE (Solution).

$Fe_2(SO_4)_3 + Aq.$ M.W. (of anhydrous salt) = 400.

(*a*)† Take of

Ferrous sulphate,	800 gr.
Sulphuric acid, 167° Tw. (sp. gr. 1.835),	83 cc.
Nitric acid, 80° Tw. (sp. gr. 1.40),	80 "
Water,	400 "

* Franz, J. pr. Chem. [2] 5, 274.
† After U. S. Pharmacopoeia, 1890.

Put the sulphuric acid into a 12-inch evaporating dish with 400 cc. of water and heat to about 90° C. Add the nitric acid and stir well. Pulverize the ferrous sulphate, and divide it into 4 or 5 portions, adding 1 portion at a time to the hot acid. Stir well after each addition, waiting until the effervescence quiets down and the ferrous sulphate is in solution before adding the next portion. Test the solution by adding to it while hot a drop or two of nitric acid; if red fumes are evolved, add more nitric acid until this evolution of fumes ceases. Heat to boiling until all nitrous fumes are expelled and the solution is a deep reddish brown color. Concentrate until the density at 15° C. is 130° Tw. (sp. gr. 1.1650), and preserve as a liquid.

Reaction:

$$6\,FeSO_4 \cdot 7\,H_2O + 3\,H_2SO_4 + 2\,HNO_3 = 3\,Fe_2(SO_4)_3 + 46\,H_2O + 2\,NO.$$

(*b*) Take of

Ferric hydrate,	200 gr.
Sulphuric acid, 167° Tw. (sp. gr. 1.835),	190 cc.
Water,	300 "

Warm the acid and water in a 12-inch evaporating dish, and add the ferric hydrate slowly, while stirring actively. When all action ceases, decant from any residue, and if the density be over 130° Tw. (sp. gr. 1.650), dilute with water to that strength.

Properties:

Ferric sulphate, obtained by evaporating the above solution to dryness, is a white anhydrous substance which readily forms basic salts of uncertain composition. The anhydrous salt dissolves very slowly in water, but the addition of a small quantity of ferrous sulphate hastens the solution very much.

Dilute solutions decompose when heated, but if concentrated will not decompose even when boiled. The hydrated salt is very soluble in water, and the solution has a strong acid reaction.

The specific gravity of the aqueous solution at 15° C. containing

10%	of the	salt	is	1.096.*
20%	"	"		1.205.
30%	"	"		1.331.
40%	"	"		1.478.
50%	"	"		1.650.

---

43. BASIC FERRIC SULPHATE (Solution).

$Fe_4(SO_4)_5(OH)_2 + Aq.$

Take of

Ferrous sulphate crystals,	1080 gr.
Sulphuric acid, 168° Tw. (sp. gr. 1.840),	52 cc.
Nitric acid, 67° Tw. (sp. gr. 1.335),	142 "
Water,	1500 "

Put the ferrous sulphate into a 14-inch evaporating dish under the hood. Mix the sulphuric acid with the ferrous sulphate, and then slowly add the nitric acid, diluted with 50 cc. of water, in small portions at a time, stirring actively. Carry on the reaction at the ordinary temperature of the room at first, but when the evolution of nitrous gases slackens, heat the dish on the water bath as long as nitrous fumes escape. If the action becomes very violent, add a little cold water to moderate it. Too violent an action tends to form insoluble basic sulphates.

The evolution of red fumes of nitric oxide is very copious

* GERLACH, Zeit. anal. Chem. **28**, **494**.

during the reaction. After the nitric oxide is all removed by heating, the product should be a dull yellow paste or a dark red liquid, according to the time of heating and the quantity of water added during the reaction. Add sufficient water to bring the density to 90° Tw. at 17.5° C., and let it stand and settle. Decant the clear solution from any residue, and preserve as a liquid, protected from air and from strong light.

[J. W. SMITH, private communication.]

Reaction:

$$12\ Fe_2SO_4{\cdot}7\ H_2O + 3\ H_2SO_4 + 4\ HNO_3 = 3\ Fe_4(SO_4)_5(OH)_2 + 86\ H_2O + 4\ NO.$$

Properties:

Basic ferric sulphate is a deep red liquid of strongly acid reaction. It should give no precipitate in dilute solution with silver nitrate nor with potassium ferricyanide, though the latter may impart a blue color to the liquid. The solution is stable only when concentrated. This salt frequently forms the major part of commercial "nitrate of iron" solutions, which are made up of mixtures of normal and basic ferric sulphates. It is used to a small extent in medicine, but chiefly in dyeing silks black.

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44. FERROUS AMMONIUM SULPHATE.

$FeSO_4(NH_4)_2SO_4{\cdot}6\ H_2O$. M.W. = 392.

Take of

Ferrous sulphate,	700 gr.
Ammonium sulphate,	332 "
Water,	2000 cc.

Dissolve the copperas and the ammonium sulphate separately in part of the water, forming concentrated solutions at 60° C. Filter if necessary, and mix the two hot solutions while stirring

well. Concentrate the solution, add 10 cc. conc. sulphuric acid, and when allowed to crystallize, clear green crystals of the double sulphate separate. Remove from the mother liquor, drain or run through the centrifugal machine, and dry quickly at a low temperature. Evaporate the mother liquor for more crystals.

Properties:

Ferrous ammonium sulphate is quite permanent in the air. Because of its constant composition, and also from the fact that its molecular weight is exactly seven times that of iron, it is used as a standard in volumetric determinations of iron.

100 parts of water at

12° C.	dissolve	17.5	parts	$FeSO_4(NH_4)_2SO_4$.*
20° "	"	21.6	"	"
30° "	"	28.1	"	"
45° "	"	36.2	"	"
60° "	"	44.6	"	"
75° "	"	56.7	"	"

Note that the above table applies only to the anhydrous salt.

The aqueous solution of the salt should not give a red color with potassium sulphocyanide.

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45. FERROUS SULPHATE.

(Copperas or Green Vitriol.)

$FeSO_4 \cdot 7\ H_2O$. M.W. = 278.

(*a*) Take of

Iron nails or turnings,	400 gr.
Sulphuric acid, 168° Tw. (sp. gr. 1.84),	400 cc.
Water,	2000 "

* TOBLER, Ann. 95, 198.

Dilute the acid with the water, and pour it over the nails in a large evaporating dish or crock. The solution of the iron is rapid, and a clear green liquid is obtained. When the action becomes slow, heat the dish until the acid is nearly neutralized and the action almost stops. Filter hot by upward filtration and suction (see FILTRATION, p. 15) to remove the sediment of carbonaceous matter and dirt. Concentrate the filtrate rapidly to 55° Tw. (sp. gr. 1.275), and allow to cool and crystallize. Pour off the mother liquor, and wash the crystals with a small quantity of water. Remove the last portion of wash water by the centrifugal machine, and dry the crystals carefully at about 25° C. in the drying closet, examining them frequently and removing them at the first indication of efflorescence. Pack in a dry bottle at once, and stopper tightly.

Concentrate the mother liquors, add 10–20 cc. of strong sulphuric acid and 2 or 3 clean bits of iron or nails, and allow the action to continue until all ferric salt is reduced to ferrous. Filter hot, and allow to crystallize again.

(*b*) In the preparation of hydrogen sulphide gas from ferrous sulphide and sulphuric acid, a solution of ferrous sulphate is obtained, which will yield very pure crystals, as follows: heat the liquid with a little ferrous sulphide to neutralize any free acid and reduce any ferric salt. Then filter at once while hot, and allow to crystallize. Separate the mother liquors and crystals, as in the previous case.

Commercial copperas may be purified by dissolving it in water (see SOLUTION, p. 5), adding 10 cc. concentrated sulphuric acid for each liter of solution, and several pieces of clean iron. When completely reduced, filter and crystallize as above.

Reactions:

$$Fe + H_2SO_4 = FeSO_4 + H_2.$$
$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

Properties:

Ferrous sulphate is very soluble. 100 parts of water at

10° C.	dissolve	60.9	parts	$FeSO_4 \cdot 7\ H_2O$.
15° "	"	70.	"	"
25° "	"	114.94	"	"
60° "	"	263.15	"	"
90° "	"	370.37	"	"
100° "	"	333.33	"	"

The following table shows the strength of aqueous solutions at 17.2° C.:

5.3° Tw.	= 5%	$FeSO_4 \cdot 7\ H_2O$,	or 2.735%	$FeSO_4$.
10.9° "	= 10%	"	" 5.47 %	"
23.1° "	= 20%	"	" 10.94 %	"
29.5° "	= 25%	"	" 13.675%	"
36.2° "	= 30%	"	" 16.41 %	"
43.1° "	= 35%	"	" 19.145%	"
50.3° "	= 40%	"	" 21.88 %	"

The pure salt forms large green crystals containing 7 H_2O. These quickly effloresce on exposure to the air, and at 110° C. lose all but one molecule of water and fall to a white powder. If not dry, the crystals oxidize very quickly on exposure, and the color becomes more or less brown or yellow. The addition of alcohol to a concentrated solution of ferrous sulphate causes a precipitation of fine crystals containing 7 molecules of water, which keep well even on exposure to the air.

The salt is known in commerce under the name of copperas, green vitriol, or protosulphate of iron.

The pure salt shows no reactions for manganese, copper, arsenic, nor zinc, which frequently contaminate the commercial article.

46. LEAD ACETATE.

(Sugar of Lead.)

$Pb(C_2H_3O_2)_2 \cdot 3\ H_2O$. M.W. = 378.

Take of

Litharge,	1000 gr.
Acetic acid, 8° Tw. (commercial No. 8),	1750 cc.

Put the litharge into a 14-inch evaporating dish, and add the acetic acid in portions of 200 cc. each, stirring with a porcelain spatula after each addition. No heating is necessary at first, but after all the acid has been added put the dish on the steam bath, and heat until all action ceases, stirring frequently.

Litharge generally contains copper as an impurity, and this shows its presence by coloring the solution of lead acetate, green. To remove the copper, put a clean piece of metallic lead into the solution, and let the dish stand quietly on the steam bath. The copper is slowly deposited on the lead; after some hours remove it, scrape and scour it until bright, and put it into the liquid again, repeating this process until the solution is free from copper. Dilute with water, let stand quietly on the steam bath to settle, and decant the clear liquid, hot, through a cloth filter, for the muddy residue is apt to clog the filter and cause very slow filtration. It is also well to remove the clear filtrate from the receiving vessel before putting the sediment on the filter, as the liquid may run through cloudy at first. Concentrated solutions of lead acetate cannot be filtered easily because of their syrupy character.

It is best to use a little less than the theoretical quantity of acid, as a slight excess of litharge tends to prevent the solution of the iron and aluminum oxides which may be present in the litharge.

After filtration evaporate the solution on the steam bath to a density of 80° Tw. (sp. gr. 1.40), adding a little acetic acid during the evaporation until the solution shows a slight acid reaction to litmus paper. Allow to cool slowly. Drain the needle-like crystals, and then use the centrifugal machine to free them from the mother liquor. If the crystals are yellowish, they must be redissolved in water and recrystallized; when white, dry them on glass plates, at a very moderate temperature in the drying closet. They must be watched very closely while drying, for if any mother liquor adheres to them they will melt, or if left in the drying closet too long they will effloresce. The mother liquor will yield more crystals if evaporated further.

Reaction:

$$PbO + 2\ C_2H_4O_2 = Pb(C_2H_3O_2)_2 + H_2O.$$

Properties:

Lead acetate forms needle-like crystals containing 3 molecules of water. The crystals effloresce in the air, and melt in their water of crystallization at 75° C. The salt is very soluble, dissolving in 1.5 parts of water at 15° C. and in one part at 40° C. The solution absorbs carbon dioxide from the air and becomes very turbid through precipitation of lead carbonate. Solutions of lead acetate will dissolve litharge, forming basic acetates, of which several are known. The pure salt is white and has a sweet taste, and hence it is known as "sugar of lead." It is very poisonous. Being one of the few soluble lead salts, it is important commercially as a source of other lead compounds. The crystallized salt should yield a nearly neutral solution in which no copper nor alumina should be found. The aqueous solution should be perfectly clear (absence of *carbonate*, *metallic lead*, etc.) and give no tests for nitric nor hydrochloric acids.

The specific gravity of an aqueous solution at 20° C. containing

5%	$Pb(C_2H_3O_2)_2 \cdot 3\,H_2O$	is	1.0311.
10%	"	"	1.0622.
15%	"	"	1.0932.
20%	"	"	1.1242.
25%	"	"	1.1543.
30%	"	"	1.1844.
35%	"	"	1.2142.
40%	"	"	1.2440.

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47. LEAD CHROMATE.

$PbCrO_4$. M.W. = 323.

(*a*) Take of

Lead nitrate,	2000 gr.
Potassium bichromate,	880 "
Water,	14 liters.

Dissolve the lead nitrate in 2500 cc. of hot water, filter if necessary, dilute the solution with 2500 cc. of cold water, and put into a large crock or precipitation jar (Fig. IX, p. 19). Dissolve the bichromate in 2500 cc. of hot water, and filter, allowing the filtrate to run into a large crock containing 6 liters of cold water. Reserve about 1 liter of each solution. Pour the cold bichromate solution into the lead nitrate solution, stirring well with a large spatula or wooden paddle. Filter off a test portion of 10 cc., and note the color; if yellow, add a drop of the reserved lead nitrate. If a precipitate falls, add about 100 cc. of the lead nitrate to the contents of the crock, stir well for 5 minutes, filter off another test portion of 10 cc., and repeat the test, adding lead nitrate to the contents of the

crock in small portions until all the bichromate has been precipitated. Then reverse the process, using the reserved bichromate as a neutralizing liquid until nearly all of one or the other reserved portion has been added and no excess of either is present. Allow to settle, and draw or siphon off the supernatant liquid. This may be evaporated for the recovery of the potassium nitrate (p. 176).

Fill up the jar with water, and stir well, thus washing the precipitate by decantation several times (p. 20) until a test of the wash water shows no nitrate present. This will require 8 or 10 or even more washings. Having drawn off the final wash water, transfer the precipitate to a cloth filter having two cloths, the upper one loose and large enough to fold in the precipitate, forming a bag in which it may be pressed in the screw press (p. 18) after the water has drained away. Press heavily until no more water can be extracted, and remove the cake of lead chromate from the cloth, break into cubes three-fourths of an inch on a side, and dry on glass plates in the warm closet. Lead chromate prepared in this way may be used for making fused chromate (p. 124), or it may be preserved as precipitated chromate.

Reaction:

$$2\ Pb(NO_3)_2 + K_2Cr_2O_7 + H_2O = 2\ PbCr_2O_4 + 2\ KNO_3 + 2\ HNO_3.$$

(*b*) Take of

Lead acetate,	2000 gr.
Potassium bichromate,	1550 "
Water,	18 liters.

Dissolve the lead acetate in 3 liters of water, filter, and put into a large precipitation jar (p. 19). Dissolve the bichromate in 15 liters of water, and filter. Mix these solutions in the

same way and with the same precautions as described in (*a*). Wash and dry the precipitated chromate as above.

Reaction:

$$2\ Pb(C_2H_3O_2)_2 \cdot 3\ H_2O + K_2Cr_2O_7 = 2\ PbCrO_4 + 2\ KC_2H_3O_2 + 2\ C_2H_4O_2 + 5\ H_2O.$$

Properties:

Lead chromate, as above prepared, is an orange yellow powder, very insoluble in water and in acetic acid. It dissolves in strong nitric acid and in caustic potash solution, and is decomposed by hot hydrochloric and sulphuric acids. It fuses at a red heat unchanged, but at higher temperature gives off oxygen. This liberation of oxygen occurs at a much lower temperature in the presence of organic substances, and on this fact depends the use of fused lead chromate in organic analysis.

The precipitated chromate is much used in the arts, *e.g.* in paints, as "chrome yellow." By mixing sodium sulphate or alum with the potassium bichromate solution before precipitating the chromate, more or less lead sulphate is thrown down with the chromate, thus lightening the color of the precipitate. In this way a number of shades of "chrome yellow" are prepared.

When boiled with dilute caustic soda solution or with lime water, lead chromate is converted into an orange or red basic lead chromate, known in the arts as "chrome orange" or "chrome red," and used as a pigment. This change is shown by the following

Reaction:

$$2\ PbCrO_4 + 2\ NaOH = PbCrO_4 \cdot PbO + Na_2CrO_4 + H_2O.$$

48. LEAD CHROMATE (Fused).

$PbCrO_4 \cdot xPbO$.

Heat thoroughly dried, precipitated lead chromate in an iron crucible until it just fuses, and pour it into an iron pan, forming a brown crystalline layer about one-eighth of an inch thick. Break this up into coarse grains, and bottle for use in organic analysis.

The temperature must not go above a low red heat, or more or less decomposition occurs. The crucible should be kept covered and its contents protected from any reducing flame. Fusion drives off any moisture and destroys any organic or carbonaceous matter present in the chromate.

A convenient way to fuse lead chromate is to use the Roessler furnace, with a crucible having a hole bored in the bottom. Place a pan under the furnace to catch the fused chromate as it flows in drops from the crucible. By this method overheating the chromate is avoided, for as soon as it liquefies, it escapes from the crucible and is cooled at once. When the fusion has once started it is only necessary to feed the dry chromate into the crucible as fast as it melts down. [J. W. SMITH.]

Properties:

Fused lead chromate is a more or less basic salt of a dark brown color and crystalline structure. It is used in organic analysis for the combustion of substances containing sulphur. The commercial product is frequently contaminated with carbonaceous matter which causes an evolution of carbon dioxide on heating.

49. LEAD NITRATE.

$Pb(NO_3)_2$. M.W. = 331.

Take of

Litharge,	2500 gr.
Nitric acid, 67° Tw. (sp. gr. 1.335),	2000 cc.
Water,	4000 "

Put the litharge into a 16-inch evaporating dish, and add 500 cc. of water, stirring to form a thin paste. Dilute the nitric acid with 1000 cc. of water, and add to the litharge in portions of about 100 cc. at a time, stirring thoroughly after each addition. When all the acid has been added, heat on the steam bath to about 90° C., and keep at that temperature for a couple of hours, stirring frequently. Add the remaining 2000 cc. of hot water to replace that evaporated, and to dissolve the nitrate completely, and stir until nothing more appears to go into solution. If the litharge contains copper, put a clean piece of metallic lead into the solution ; this causes a precipitation of the copper on the lead, which must be removed at frequent intervals and scraped and scoured clean. In two or three days the copper will nearly all be removed. Keep the lead plate in the solution while evaporating to dryness on the steam bath. When dry add about 100 cc. of strong nitric acid; let this act for a few moments, and then take up with 4 liters of hot water, heat to 90° C. or above, and filter hot on a cloth filter or by upward filtration (p. 15). Concentrate the clear filtrate to a density of 100° Tw. (sp. gr. 1.50), and let it cool very slowly. If a few cc. of nitric acid be added to the solution just before allowing it to crystallize, the crystals obtained will be transparent and colorless. If no excess of acid is present when crystallization takes place, the crystals are usually white and opaque. Recrys-

tallize the product once from water containing a little nitric acid. Decant the mother liquor from the crystals, and after draining, dry them in the warm closet. Evaporate the mother liquor for more crystals.

Reaction:

$$PbO + 2\ HNO_3 = Pb(NO_3)_2 + H_2O.$$

Properties:

Lead nitrate crystallizes in regular octahedrons, containing no water of crystallization.

1 part of lead nitrate dissolves in

2.58	parts	water	at	0° C.*
2.07	"	"	"	10° "
1.65	"	"	"	25° "
1.25	"	"	"	45° "
0.99	"	"	"	65° "
0.83	"	"	"	85° "
0.72	"	"	"	100° "

100 parts of water at

0° C.	dissolve	36.5	of	the	salt.†
10° "	"	44.4	"	"	"
20° "	"	52.3	"	"	"
30° "	"	60.7	"	"	"
40° "	"	69.4	"	"	"
50° "	"	78.7	"	"	"
60° "	"	88.0	"	"	"
70° "	"	97.7	"	"	"
75° "	"	102.6	"	"	"
80° "	"	107.6	"	"	"
85° "	"	112.5	"	"	"
90° "	"	117.4	"	"	"
95° "	"	122.3	"	"	"
100° "	"	127.0	"	"	"
104° "	"	130.9	"	"	"

* KREMERS, Pogg. Ann. **92**, 497.
† MULDER, Scheik. Verhand. **1864**, 66.

The specific gravity of the aqueous solution at 17.5° C. containing

5%	$Pb(NO_3)_2$	is	1.044.*
10%	"	"	1.092.
15%	"	"	1.144.
20%	"	"	1.200.
25%	"	"	1.263.
30%	"	"	1.333.
35%	"	"	1.409.

Saturated solution is 1.433.

It is important as furnishing a soluble lead salt which crystallizes very well and can be purified easily. When heated the salt decomposes into litharge, nitrous oxide, and oxygen. Basic nitrates may be formed by dissolving litharge in the solution of neutral lead nitrate.

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50. LEAD PEROXIDE.

PbO_2. M.W. = 239.

Take of

Lead acetate (or nitrate),	250 gr.
Bleaching powder,	400 "
Water,	4½ liters.

Dissolve the lead acetate in 1500 cc. of hot water in a 14-inch evaporating dish. Stir up the bleaching powder (calcium hypochlorite) with 3 liters of cold water, and filter with suction on cotton wool or cloth (p. 13). Slowly add about one-half of the filtered solution of bleaching powder to the hot solution of the lead salt, while stirring actively. The light-colored precipitate

* GERLACH, Zeit. anal. Chem. **27**, 283.

of lead peroxide which first separates, becomes dark brown on heating the mixture for a time. Filter off 10 cc. into a test tube, add a few drops of the bleaching powder solution to the filtrate, and warm. If a precipitate is produced in the test portion, add more of the bleach solution to the main mass of the lead salt solution. Test again, and repeat the process until all the lead has been thrown down as peroxide. Stir up well after each addition of the calcium hypochlorite liquor, and heat nearly to boiling.

Allow to settle, and decant the top liquor; stir up with warm water, and again settle and decant, repeating this process a number of times until the wash waters are free from chloride, nitrate, or acetate. Free the brown powder from adhering wash water by means of the filter pump, and dry it on a glass plate in the warm closet.

Reaction:

$$Pb(C_2H_3O_2)_2 + CaOCl_2 + H_2O = PbO_2 + 2\,HCl + Ca(C_2H_3O_2)_2.$$

Properties:

Lead peroxide is a heavy brown powder, insoluble in water, and in cold nitric or sulphuric acids. Hydrochloric acid decomposes it cold and other acids attack it when hot. Caustic soda and potash dissolve it, forming plumbate of the alkali metal. It gives up an atom of oxygen quite readily to oxidizable substances, especially when heated.

51. MAGNESIUM CHLORIDE.

$MgCl_2 \cdot 6 H_2O$. M.W. = 203.

Take of

Magnesite (powdered),	1000 gr.
Hydrochloric acid, 36° Tw. (sp. gr. 1.180),	2000 cc.
Magnesium oxide (calcined magnesia),	10 gr.
Water,	1000 cc.

Mix the magnesite in a 14-inch evaporating dish with 500 cc. of water, heat on the steam bath to about 90° C., and add the acid in small portions at a time, stirring actively and allowing the effervescence caused by each portion to subside before adding the next. When all the acid has been added, keep the solution hot for some time, on the steam bath, until all action ceases. Test with litmus paper, and, if acid, add a little excess of magnesite until neutral. Dilute with 500 cc. of water, add 30–40 cc. of chlorine water, and keep warm for an hour, stirring frequently. Finally add 10 gr. of magnesium oxide (calcined magnesia), and stir well while hot. After digesting an hour, filter hot on cloth or paper. Evaporate the clear filtrate of magnesium chloride on the steam bath to a density of 60° Tw. (sp. gr. 1.300) in the hot solution, and allow to cool. It is best to separate the crystals from the mother liquor, in the centrifugal machine; or they may be drained in a funnel covered with a watch glass.

The solution of magnesium chloride should not be boiled during concentration, as this may cause decomposition, magnesium oxychloride being formed and hydrochloric acid escaping.

By the above method, the product may not be free from calcium salts, owing to the calcium carbonate in the magnesite.

For a pure salt the purified magnesia alba* or calcined magnesia of commerce may be used.

Reaction:

$$MgCO_3 + 2\,HCl = MgCl_2 + H_2O + CO_2.$$

Properties:

Magnesium chloride crystallizes in white deliquescent crystals containing $6\,H_2O$. It is very soluble in water, dissolving in 0.6 parts of cold and in 0.3 parts of hot water.

The specific gravity of the aqueous solution at 15° C. containing

1%	$MgCl_2$	is	1.0084.†
5%	"		1.0422.
10%	"		1.0859.
15%	"		1.1311.
20%	"		1.1780.
25%	"		1.2274.
30%	"		1.2794.
35%	"		1.3340.

Anhydrous magnesium chloride cannot be prepared by heating the crystallized salt, because of the above-mentioned decomposition. But the double chloride of ammonium and magnesium $MgCl_2 \cdot NH_4Cl \cdot 6\,H_2O$, formed by adding the required quantity of ammonium chloride to the magnesium chloride solution, may be evaporated to dryness without loss of hydrochloric acid. By heating this double salt, the ammonium chloride passes off as volatile matter, leaving the magnesium chloride in the fused condition.

Magnesium chloride is used to a considerable extent as a stiffening material in textile industries. The pure salt is used

* Magnesia alba is a basic magnesium carbonate of somewhat varying composition, but approximating $Mg(OH)_2 \cdot 3\,MgCO_3 \cdot 3\,H_2O$.

† Gerlach, Zeit. anal. Chem. **8**, 281.

in the laboratory for "magnesia mixture," etc. It should dissolve clear in absolute alcohol (absence of *sulphates*, *sodium salts*, etc.), and give no precipitate with ammonium chloride and ammonia (absence of *phosphoric acid*), nor with hydrogen sulphide, ammonium chloride, ammonium oxalate, nor ammonia (absence of *heavy metals*, *lime*, etc.).

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52. MAGNESIUM SULPHATE.

(Epsom Salts.)

$MgSO_4 \cdot 7\ H_2O$. M.W. = 246.

(*a*) Take of

Magnesite (powdered),	1000 gr.
Sulphuric acid, 166° Tw. (sp. gr. 1.830),	680 cc.
Water,	4000 "

Put the powdered magnesite into a 16-inch evaporating dish, and add 2 liters of water to form a thin cream. Then add, while stirring actively, about 50 cc. of the sulphuric acid, and wait until the effervescence moderates before adding another portion of acid. When about two-thirds of the acid have been added in this way, dilute the solution with another liter of water, and heat on the steam bath while adding the remainder of the acid in portions of about 50 cc. When all the acid has been added, dilute with another liter of water, and heat on the steam bath for an hour or two, stirring frequently. Test the solution with litmus paper, and, if acid, add a little more powdered magnesite and boil the solution; or add a little magnesia alba (basic magnesium carbonate) until the solution is neutral. Allow to

stand to settle, and, if necessary, decant the clear solution of magnesium sulphate through a filter. Evaporate the solution to a density of 66° Tw. (sp. gr. 1.330), and allow to cool slowly to crystallize. Drain the crystals, or put them through the centrifugal machine; dry on a glass plate in the warming oven at a temperature of about 25° C.

No excess of acid should be used, but rather a slight excess of the magnesite, to make a neutral solution. The addition of a small quantity of precipitated magnesium carbonate or magnesium oxide assists in the precipitation of iron or alumina. Since magnesite contains calcium carbonate, a slight trace of calcium sulphate is usually found in the crystals of epsom salts.

Reaction:

$$MgCO_3 + H_2SO_4 = MgSO_4 + H_2O + CO_2.$$

(*b*) The mineral dolomite may be used instead of magnesite, but in this case a larger proportion of calcium sulphate contaminates the salt. By calcining the dolomite, and then extracting with a small amount of hydrochloric acid, the major part of the calcium oxide may be dissolved out, leaving a residue of fairly pure magnesium oxide, which may then be dissolved in sulphuric acid.

Properties:

Magnesium sulphate forms small, clear crystals containing 7 H_2O when crystallized at ordinary temperatures, but only 6 H_2O when deposited from hot solution (over 40° C.). The crystals melt in their "water of crystallization" when heated to 70–80° C., and lose 6 H_2O above 150° C. At 200° C. the salt becomes anhydrous.

100 parts of water at

0°	C.	dissolve	26.9	parts	$MgSO_4$.*
10°	"	"	31.5	"	"
20°	"	"	36.2	"	"
30°	"	"	40.9	"	"
40°	"	"	45.6	"	"
50°	"	"	50.3	"	"
60°	"	"	55.0	"	"
70°	"	"	59.6	"	"
80°	"	"	64.2	"	"
90°	"	"	68.9	"	"
100°	"	"	73.8	"	"
108°	"	"	77.7	"	"

The specific gravity of the aqueous solution at 15° C. containing

1%	$MgSO_4$	is	1.01031.†
5%	"	"	1.05154.
10%	"	"	1.10529.
15%	"	"	1.16222.
20%	"	"	1.22212.
25%	"	"	1.28478.

The aqueous solution should give no coloration nor precipitate with hydrogen sulphide, nor should potassium ferrocyanide cause any change. (*Iron, copper, zinc.*) Only a trace of *chloride* should be present. Small traces of *arsenic* are often found in commercial samples.

Magnesium sulphate is extensively used in the textile industries and in dyeing; also in medicine and to some extent in agriculture.

* Mulder, Scheik. Verhand. **1864**, 52.
† Gerlach, Zeit. anal. Chem. **8**, 287.

53. MANGANESE CARBONATE.

$MnCO_3$. M.W. = 115.

This substance may be prepared from the waste liquors from the preparation of chlorine. Purify the manganous chloride solution, as described under "Manganese Chloride" (p. 135). Put the purified solution into a precipitation jar (Fig. IX, p. 19), and add either sodium carbonate or ammonium carbonate solution until a test filtered off gives no precipitate with a drop of the carbonate solution. Let it settle, and draw off the supernatant liquid. Wash the precipitate with distilled water by decantation (p. 20) until free from soluble chlorides and carbonate. Finally decant the last wash water, and free the precipitate from water as quickly as possible on a Büchner funnel (p. 14). Dry in the warm closet at 40° C., and bottle as soon as dry. By exposure to the air the wet carbonate is oxidized more or less and becomes darker. Hence, washing by decantation makes the product a lighter color.

Reaction:

$$MnCl_2 + (NH_4)_2CO_3 = MnCO_3 + 2\,NH_4Cl.$$

Properties:

Manganese carbonate forms a pale pink powder, easily soluble in acids (even in acetic acid), but insoluble in water. When heated to 300° C. it gives off carbonic acid, and if exposed to the air at this temperature, it absorbs oxygen, forming oxides of manganese.

54. MANGANESE CHLORIDE.

$MnCl_2 \cdot 4\ H_2O$. M.W. = 198.

The most convenient source of this salt is the acid waste liquor from the preparation of chlorine by the use of pyrolusite and hydrochloric acid, as described under "Aluminum Chloride" on page 40. Evaporate the acid liquors to dryness on the steam bath to remove all excess of acid. Take up with water, and boil until all soluble matter is in solution. Take about one-eighth of the solution, and add to it sodium carbonate to precipitate manganese carbonate and ferric hydrate. Filter, and wash the precipitate with water, by decantation (p. 20), until free from sodium salts. Add this precipitate to the main mass of the solution, and boil. Iron is precipitated as hydrate, while a corresponding quantity of manganese carbonate goes into solution as chloride. After boiling half an hour, dilute the solution if necessary, and filter off the iron hydrate and insoluble residue. If the solution of manganese chloride contains copper, this may be precipitated by passing hydrogen sulphide into the solution. After filtering, evaporate to a density of 94° Tw. (sp. gr. 1.470), and allow to stand quietly to crystallize. Drain the crystals, and dry in a desiccator over sulphuric acid.

If the solution is contaminated with calcium or magnesium chloride, the manganese may be precipitated by adding ammonia and ammonium sulphide, avoiding excess. After filtration, wash the precipitated manganese sulphide with water until free from ammonia salts, and dissolve in hydrochloric acid, using no large excess of acid. Boil off the hydrogen sulphide, and filter if necessary. Crystallize as above described.

Properties:

Manganese chloride forms pale red crystals which deliquesce in moist air.

100 parts of water at

8° C.	dissolve	151	parts	of the	crystallized	salt.*
31.25° "	"	265	"	"	"	"
62.5 ° "	"	641	"	"	"	"
87.5 ° "	"	641	"	"	"	
106.25° "	"	656	"	"	"	"

It is also soluble in absolute alcohol, from which it may be crystallized.

The specific gravity of an aqueous solution at 15° C. containing

5%	of $MnCl_2$	is	1.045.†
10% "	"	"	1.091.
20% "	"	"	1.189.
25% "	"	"	1.245.
30% "	"	"	1.306.
40% "	"	"	1.443.
45% "	"	"	1.514.

Solutions of manganous chloride obtained in the generation of chlorine for technical purposes are the chief sources of manganese salts.

The commercial product is often contaminated with sulphate.

* BRANDES, Pogg. Ann. **22**, 263.

† GERLACH, Zeit. anal. Chem. **28**, 476.

55. MANGANESE SULPHATE.

$MnSO_4 \cdot 4\ H_2O$. M.W. = 223.
$MnSO_4 \cdot 5\ H_2O$. M.W. = 241.

Take of

Pyrolusite (powdered),	2000 gr.
Sulphuric acid, 166° Tw. (sp. gr. 1.830),	1340 cc.

Mix the pyrolusite with the concentrated acid to form a thick paste. Transfer to a Battersea G crucible, and heat in the Roessler furnace, stirring with an iron rod all the time while heating, to prevent spurting. After some time the mass becomes solid; raise the heat to a bright red and keep so for an hour. This decomposes the ferrous sulphate into ferric oxide, and sulphuric anhydride which volatilizes. Allow the crucible to cool, and break out the fused mass. Crush to a coarse powder, and lixiviate with hot water in a 14-inch evaporating dish. Filter, and wash the brown mud with two or three wash waters, adding these to the main filtrate. Concentrate the solution of manganous sulphate to a volume of 3 liters. To remove the iron, take about one-eighth of the solution and add to it a solution of sodium carbonate as long as a precipitate falls. Allow to settle, decant the liquor, and wash a number of times by decantation (p. 20), until no sulphate can be detected in the wash water. The precipitate should be kept under water most of the time during washing; hence decantation is preferable to filtration in this instance. Add the manganese carbonate thus obtained to the main body of the solution, and stir well while heating to boiling. This precipitates the iron from any ferrous sulphate which has not been destroyed

during the ignition. Filter, and evaporate the filtrate until the solution has a small bulk (about 1800 cc.), and filter off any trace of iron which may have separated. Put the solution into a shallow 8-inch evaporating dish, place in a desiccator over sulphuric acid, and leave for several days until it forms a solid cake of crystals. Break up the crystals, and drain from any adhering mother liquor. The draining cone should be covered with a damp cloth to prevent efflorescence of the top crystals. Bottle as soon as dry to the touch, and stopper well. Keep in a moderately cool place.

Instead of crystallizing in a desiccator, the solution of manganese sulphate may be put in the warm closet at a temperature of 30° C., and left there several days until a crystalline mass forms in it. But in this case the crystals form with 4 H_2O instead of with 5 H_2O. When crystallized at a very low temperature, a salt $MnSO_4 \cdot 7\ H_2O$ forms.

Reaction:

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O.$$

Properties:

Manganese sulphate, as usually prepared, forms pale pink crystals which are easily soluble in an equal weight of water at 19° C. The solubility varies according to the number of molecules of crystal water, but is greatest at about 55° C., when the solution contains 74.7 parts of anhydrous salt in 100 parts of water.*

The specific gravity of an aqueous solution at 15° C. containing

* For tables of solubility of the various crystallized sulphates of manganese, see MULDER, Scheik. Verhand. **1864**, 137. LINEBARGER, Am. Chem. J. **15**, 225.

5%	of the anhydrous	salt	is	1.050.*
10%	"	"	"	1.1035.
15%	"	"	"	1.1605.
20%	"	"	"	1.2215.
25%	"	"	"	1.2870.
30%	"	"	"	1.3575.

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56. MERCURIC CHLORIDE.

(Corrosive Sublimate.)

$HgCl_2$. M.W. = 271.

(*a*) Take of

Mercuric sulphate (dry),	100 gr.
Sodium chloride (dry),	50 "
Pyrolusite (powdered and ignited),	5 "

Mix the finely powdered materials very thoroughly, and introduce the mixture into a retort whose neck has been cut off at about the middle, in order to afford a wide opening. Bury the body of the retort up to the neck in dry sand contained in an iron dish. Place the apparatus under a hood with a good draught, and heat gently at first until moisture is all removed, warming the retort neck with a lamp to drive out the water vapor. Then raise the heat of the sand bath, place a wide-mouthed bottle over the retort neck, and heat as long as any sublimate comes over, taking care that the retort neck does not become clogged.

Allow the retort to cool slowly, and then carefully rake out the sublimate from the neck, and bottle it at once.

The vapors of mercuric chloride are very poisonous, and much care must be taken not to inhale them nor to allow them to

* GERLACH, Zeit. anal. Chem. **28**, 475.

come in contact with the skin. The hood should be kept closed and a good draught insured. Neither should the salt be handled with bare hands.

Reaction :

$$HgSO_4 + 2\ NaCl = HgCl_2 + Na_2SO_4.$$

The pyrolusite is added to furnish a little free chlorine gas in the retort, which prevents the formation of mercurous chloride (calomel).

Instead of using a retort as above, the mixture may be heated in a 6-inch evaporating dish, over which a 5½-inch funnel is inverted, fitting close to the sides of the dish. By careful heating on the sand bath, the mercuric chloride will condense on the funnel walls, and may be removed readily when the operation is ended.

(*b*) According to Wagner* the basic mercuric sulphate (*turpeth mineral*) may be treated with hydrochloric acid, according to the proportions indicated in the following reaction :

$$(3\ HgO)\cdot SO_3 + 2\ HCl = HgCl_2 + H_2SO_4 + 2\ HgO.$$

The mercuric chloride may be crystallized out of the sulphuric acid solution.

(*c*) From residues :

Take the residues of mercury salts that collect in the laboratory, and evaporate to dryness on the steam bath. Treat with *aqua regia*, and again evaporate to dryness. Put the dry mass into a 6 or 8-inch evaporating dish, place it on the sand bath with a large funnel inverted over it, and heat until the mercuric chloride has sublimed into the funnel. Dissolve about one-sixth of the sublimate in hot water, and add caustic soda. Wash the

* Dingl. J. **186**, 135.

precipitated oxide with hot water, and dry. Mix it with the remainder of the sublimate, and resublime the mixture in a long-necked flask, whose mouth is covered with a watch glass. Break out the bottom of the flask by placing it, while hot, on a wet cloth, and carefully scrape the sublimate from the glass.

Properties:

Mercuric chloride forms a white crystalline mass, or, when crystallized from solution, long needles. It should be kept in a dark place or in amber-colored glass bottles. It is soluble in water, forming a solution with acid reaction.

100 parts of water at

0°C.	dissolve	5.73	parts	$HgCl_2$.*
10° "	"	6.57	"	"
20° "	"	7.39	"	"
30° "	"	8.43	"	"
40° "	"	9.62	"	"
50° "	"	11.34	"	"
60° "	"	13.86	"	"
70° "	"	17.29	"	"
80° "	"	24.30	"	"
90° "	"	37.05	"	"
100° "	"	53.96	"	"

Mercuric chloride is soluble in dilute hydrochloric and nitric acids, and in alcohol and ether. It is very poisonous, the best antidote being white of egg. It is much used as an antiseptic and preservative agent, and as a laboratory reagent. Commercial samples are often contaminated with arsenic and frequently leave an insoluble residue on solution. It is known in commerce as corrosive sublimate.

*Poggiale, Ann. Chim. Phys. [3] 8, 468.

57. MERCURIC IODIDE.

(Biniodide of Mercury.)

HgI_2. M.W. = 454.

Take of

Mercuric chloride,	100 gr.
Potassium iodide,	123 "
Water,	6000 cc.

Dissolve the mercuric chloride and the potassium iodide each in 2 liters of water, and filter the solutions separately, allowing the filtrates to run simultaneously into a precipitation jar (p. 19), containing 2 liters of water, while stirring the contents of the jar actively to cause thorough mixture. Allow the scarlet precipitate of mercuric iodide to subside, and decant the clear liquor. Wash by decantation several times with cold distilled water, until a test of the wash water shows only a slight turbidity with silver nitrate. Remove excess of water as far as possible by use of the suction filter (p. 13), and dry the powder in a dark place, at a temperature not above 35° C. Preserve in a bottle of amber glass and protect from light.

No excess of either mercuric chloride or potassium iodide should be used in the preparation, because the mercuric iodide is soluble in either of these solutions. For this reason the solutions must be mixed with the water simultaneously and with active stirring.

Reaction:

$$HgCl_2 + 2\ KI = HgI_2 + 2\ KCl.$$

Properties:

Mercuric iodide forms a scarlet amorphous powder, which is not changed by exposure to the air. It is very slightly soluble

in water, but dissolves readily in sodium hyposulphite (thiosulphate) and in alkaline iodides. It is also soluble in alcohol. It melts at about 238° C., and volatilizes at higher temperatures, leaving no residue.

It is used to a small extent in medicine, and in the laboratory for the preparation of Nessler's solution for detecting ammonia.

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58. MERCURIC NITRATE.

$Hg(NO_3)_2 \cdot \frac{1}{2} H_2O$. M.W. = 333.

Take of

Mercury,	100 gr.
Nitric acid, 50° Tw. (sp. gr. 1.250),	180 cc.

Put the mercury into a 500-cc. flask, and add the nitric acid in portions of 25 cc. at a time, allowing the action caused by one portion to subside before adding the next. If the reaction does not start readily at first, warm the flask gently on the water bath, and if the heat of the reaction is not sufficient to keep the temperature rather high, leave the flask on the water bath until all the acid has been added. When the mercury is nearly all dissolved, continue the heating on the sand bath, and finally boil up well until a test portion of the liquid shows no precipitate with sodium chloride solution. Should a precipitate fall in this test, showing the presence of mercurous salt, add a few drops of concentrated nitric acid, and boil again until all mercurous salt is converted to the mercuric state. Allow the flask to stand quietly in a warm place until any sediment has deposited, and decant the clear solution, or filter on glass wool (p. 13). Evaporate the liquid somewhat and allow to cool.

Drain the crystals of mercuric nitrate in a covered funnel, and dry in a desiccator over sulphuric acid. Bottle as soon as dry.

Reaction:

$$3\,Hg + 8\,HNO_3 = 3\,Hg(NO_3)_2 + 4\,H_2O + 2\,NO.$$

Properties:

Mercuric nitrate forms deliquescent crystals which decompose when treated with water, forming basic salts, and finally going completely to mercuric oxide. The crystals dissolve in a very small amount of water, forming a concentrated solution which is much more stable than when diluted. The salt dissolves without decomposition in water acidified with nitric acid.

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59. MERCURIC SULPHATE.

$HgSO_4$. M.W. = 296.

Take of

Mercury,	100 gr.
Sulphuric acid, 166° Tw. (sp. gr. 1.830),	75 cc.

Put the mercury into a 250 cc. flask, add the concentrated sulphuric acid, and heat *gently* on the sand bath under the hood. When the reaction starts, an evolution of sulphurous acid fumes takes place. When this fuming ceases, remove a drop of the liquid on a stirring rod, dissolve it in 2 cc. of distilled water in a test tube, and add a drop of sodium chloride solution. If a precipitate falls, or the liquid becomes milky, mercurous salt is present. In this case add 5–10 cc. more of the concentrated sulphuric acid to the contents of the flask; heat again for some time, and repeat the test.

When free from mercurous salts, pour the solution into a 4-inch evaporating dish, and allow to cool in a desiccator. Small white scales or plates of mercuric sulphate are deposited from this concentrated acid solution. Filter on a fine platinum cone with suction (p. 13), and dry on a porous porcelain plate. Or the solution of mercuric sulphate may be evaporated to dryness carefully, in the 4-inch evaporating dish under the hood, in which case a white crystalline mass is obtained.

Reaction:

$$Hg + 2\ H_2SO_4 = HgSO_4 + 2\ H_2O + SO_2.$$

Properties:

Mercuric sulphate is soluble in dilute sulphuric acid, but is not soluble in cold water. By boiling with water it is converted into a yellow basic mercuric sulphate $(3\ HgO)SO_3$, which is used in pharmacy under the name of *turpeth mineral.*

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60. MERCURIC SULPHIDE.

(Vermilion.)

HgS. M.W. = 232.

(*a*) Take of

Mercury,	150 gr.
Sulphur (powdered),	57 "
Caustic potash,	38 "
Water,	300 cc.

Put the mercury and the sulphur into a dry 8-inch mortar, and triturate until the ingredients are thoroughly incorporated. Dissolve the caustic potash in the 300 cc. of water in a 10-inch

evaporating dish, and add the contents of the mortar. Heat to 45° C. and keep at this temperature for several hours, stirring very thoroughly with a spatula at frequent intervals, and keeping the volume of water constant for the first 2 hours. The temperature must be carefully regulated not to exceed 45° C. nor to fall below 40° C.

In the course of 2 or 3 hours the mass becomes brown, and then gradually turns a bright red. When the desired vermilion color is acquired, which is usually after 6 or 8 hours' heating, pour into a precipitation jar (p. 19) full of water, and wash thoroughly by decantation until entirely free from caustic. Filter with suction on a Büchner funnel (p. 14), and dry on glass plates in the drying closet. The heat must be carefully regulated not to exceed 45° or 50° C., or the product will turn brown. For the same reason, the caustic must be washed away as quickly as possible after the color reaches its brightest shade.

The reactions occurring are rather obscure, but the following represents the changes approximately.

$$Hg + 8\,S + 4\,KOH + O = HgS + K_2S_5 + K_2S_2O_3 + 2\,H_2O.$$

Properties:

Mercuric sulphide as thus prepared, forms a heavy, brilliant scarlet powder, insoluble in water, alkalies, and dilute acids. It dissolves in very concentrated nitric acid and in *aqua regia*. When heated to a high temperature, the color changes to black, but when heated out of contact with the air, it sublimes without any apparent change, leaving some black residue.

(*b*) Vermilion is much used as a scarlet paint, and for this purpose it is best prepared in the "dry way" by subliming the black sulphide called *ethiops*, which is prepared by gently heating mercury and sulphur in iron pans.

61. MOLYBDENUM TRIOXIDE.

MoO_3. M.W. = 144.

(*a*) From residues :

Take the residues of ammonium phospho-molybdate which collect in analytical work and evaporate to dryness on the steam bath. Pulverize the dry mass, and extract with concentrated ammonia water, stirring frequently and warming gently. Decant through a filter and add to the filtrate one-fourth its volume of "magnesia mixture" ($MgCl_2 + NH_4Cl + NH_4OH$). Cover the dish and let it stand quietly a day or two, and then filter off the precipitated ammonium-magnesium phosphate. Cautiously add concentrated nitric acid in excess, to the diluted filtrate. At first the precipitate redissolves on stirring, but as the quantity of acid is increased, it becomes permanent. When a test portion of the liquor after filtration gives no further precipitate with acid, put the dish aside and let the yellowish white precipitate of molybdenum trioxide settle. Decant the supernatant liquid, and wash the precipitate with water until free from ammonia. Remove excess water by using the suction pump, and dry on a glass plate at 30° C.

The recovered molybdic trioxide should be subjected to the following tests : the solution in dilute ammonia must be clear, and the addition of ammonium sulphide should produce no precipitate ; if 5 gr. of the acid be dissolved in 10 cc. of concentrated ammonia diluted with 20 cc. of water, and 75 cc. of nitric acid added, no precipitate should result after standing 3 hours in a warm place.

(*b*) From molybdenite : *

* BRUNNER, Dingl. J. **150**, 372.

Take of

Molybdenite,	200 gr.
Quartz sand,	200 "
Ammonia water (concentrated),	a sufficient quantity.
Ammonium sulphide,	
Nitric acid (concentrated),	

Mix the molybdenite and the quartz sand in a mortar until reduced to a fine powder. Put this mixture into a shallow iron or earthenware dish in convenient quantities, and heat to a low red heat, stirring frequently. The mass changes color, and finally becomes yellow or white, owing to the oxidation of the molybdenite. Cool, and digest in a flask with concentrated ammonia water, until the yellow molybdic acid is dissolved. Decant through a filter. Roast the residue, and extract with ammonia, adding this solution to the first. Add a little ammonium sulphide to precipitate any copper present. Filter, and evaporate the filtrate to dryness. Ignite at a very faint red heat until the residue is white or pale yellow. Add concentrated nitric acid, heat in a covered dish on the steam bath for 2 or 3 days, and then evaporate to dryness. This converts any phosphoric acid to the tribasic form. Take up in dilute ammonia, and filter on a folded filter. Add to the filtrate 3 times its weight of nitric acid (sp. gr. 1.200), and let the solution stand in a warm place for several days. Any phosphoric acid in the solution will precipitate during this period as ammonium phospho-molybdate. Filter or decant, and treat the filtrate with an excess of moderately dilute nitric acid, as described in (*a*), to precipitate the oxide.

Properties:

Molybdenum trioxide is a nearly white powder having a slight yellow tinge. It is very slightly soluble in cold water,

but is easily dissolved by alkaline solutions. The commercial products usually contain more or less ammonium nitrate, which is recognized by boiling with caustic soda and noting the odor of ammonia.

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62. NICKEL NITRATE.

$Ni(NO_3)_2 \cdot 6\ H_2O$. M.W. = 301.

Take of

Metallic nickel,	100 gr.
Nitric acid, 68° Tw. (sp. gr. 1.34),	395 cc.
Water,	400 "

Put the nickel into a 10-inch evaporating dish (under the hood), and add 200 cc. of water. Slowly add about 100 cc. of the nitric acid, warm if necessary till the reaction is well started, then remove the lamp, and let the solution of the metal proceed until the action becomes slow. Then add about 100–150 cc. more of the acid, with 100 cc. of water, and let this react until nearly neutralized, and finally add the remainder of the acid with another 100 cc. of water. When the metal is nearly all in solution, heat until all is dissolved, or the action ceases. Should a residue remain undissolved after heating and after all reaction has ceased, decant the liquid (nickel nitrate) through an asbestos filter (p. 13), and wash the residue with warm water, adding the wash waters to the filtrate. Dilute the solution of nickel nitrate with twice its bulk of water, and pass into it a stream of hydrogen sulphide until no more precipitate forms. Filter off the precipitated copper, arsenic, and bismuth sulphides, using suction, but without washing the precipitate.

Concentrate the filtrate until its bulk is about 500–600 cc., and allow it to cool very slowly to crystallize. Dry the crystals

in the desiccator over sulphuric acid. The mother liquor may be concentrated further for more crystals.

Reaction:

$$3\ Ni + 8\ HNO_3 = 3\ Ni(NO_3)_2 + 4\ H_2O + 2\ NO.$$

Properties:

Nickel nitrate forms large dark green crystals which are soluble in 2 parts of water at ordinary temperature. The salt is also soluble in alcohol. It crystallizes with 6 H_2O, and is not deliquescent in dry air. At 56.7° C. the crystals melt in their "water of crystallization."

Specific gravity of an aqueous solution at 17° C. containing

5%	nickel	nitrate	is	1.0463.*
10%	"	"	"	1.0903.
15%	"	"	"	1.1375.
20%	"	"	"	1.1935.
25%	"	"	"	1.2534.
30%	"	"	"	1.3193.
35%	"	"	"	1.3896.
40%	"	"	"	1.4667.

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63. OXALIC ACID.†

$C_2H_2O_4 \cdot 2\ H_2O$. M.W. = 126.

(*a*) Take of

Commercial oxalic acid,	1000 gr.
Hydrochloric acid, 15° Tw. (sp. gr. 1.075),	400 cc.

Heat the dilute hydrochloric acid in a 12-inch evaporating dish, and add the oxalic acid slowly while stirring, until a

* Franz, J. pr. Chem. [2] 5, 295.

† After Stolba.

saturated solution is obtained. Allow to stand on the steam bath a few moments to settle, and decant the clear liquid carefully from the residue. Cool the solution rapidly, stirring actively to form small crystals. Filter with suction on the Büchner funnel (p. 14), and wash the crystalline meal with water, as cold as can be conveniently had, to remove adhering hydrochloric acid. Redissolve in twice its weight of distilled water, filter to remove any dirt, and allow the liquid to cool slowly without stirring. Drain the crystals from the mother liquor, and dry in a desiccator at the ordinary temperature of the room, taking care to turn the mass over several times while drying. The hydrochloric acid decomposes any oxalates present, and converts their bases to chlorides, which remain in solution while the oxalic acid crystallizes out.

(*b*) From starch:

Oxalic acid may be prepared by treating 1 part of starch with 8 or 9 parts of nitric acid at 67° Tw. (sp. gr. 1.335), adding the acid gradually, and heating to the boil until all nitrous fumes have escaped. Concentrate the resulting solution to about one-sixth its original volume, and allow to crystallize. Recrystallize several times from distilled water.

The reaction is very violent and the yield is uncertain. The process may be represented by an equation, but it is by no means quantitative:

$$2\ C_6H_{10}O_5 + 18\ HNO_3 = 6\ C_2H_2O_4 + 13\ H_2O + 9\ N_2O_3.$$

Oxalic acid is made on a technical scale, by heating sawdust with a mixture of caustic potash and soda, extracting the fused mass with water, and precipitating calcium oxalate by adding "milk of lime." The calcium oxalate is then decomposed with sulphuric acid, and the solution of oxalic acid filtered from the residue of calcium sulphate.

Properties:

Oxalic acid forms transparent crystals containing 2 molecules of crystal water. When heated to 70° C., the water is slowly given off and the crystals become opaque. Between 95° and 100° C., they melt in their crystal water.

Oxalic acid is very soluble in water, and its solution is a strong reducing agent.

100 parts of water at

10° C.	dissolve	8.	parts	oxalic	acid.*
20° "	"	13.9	"	"	"
30° "	"	23.	"	"	"
40° "	"	35.	"	"	"
50° "	"	51.2	"	"	"
60° "	"	75.	"	"	"
70° "	"	117.7	"	"	"
80° "	"	204.7	"	"	"
90° "	"	345.	"	"	"

The acid is very poisonous. It is used extensively in bleaching, dyeing, and calico printing in certain inks and dyes, and in various cleansing and polishing mixtures.

For use in analytical work, the acid must be free from sulphuric acid, ammonia, and heavy metals. The presence of potassium must also be guarded against.

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64. PHOSPHORUS OXYCHLORIDE.†

$POCl_3$. M.W. = 153.5.

Take of

Phosphorus trichloride,	500 gr.
Potassium chlorate,	160 "

* ALLUARD.

† DERVIN, Compt. Rend. **97**, 576; J. pr. Chem. [2] **28**, 382.

Put the 500 gr. of phosphorus trichloride into a 1500 cc. tubulated retort, and connect a return cooler with the neck. Dry the 160 gr. of potassium chlorate, pulverize it very fine, and introduce it through the tubulature in 4-gr. portions at a time, waiting until the vigorous action has quieted, before adding another portion. Then turn down the neck of the retort, fix a thermometer in the tubulature, and distill off the phosphorus oxychloride, keeping separate, as pure, that part of the distillate that comes over between 106° and 110° C. The earlier fractions contain some free chlorine. It is best to heat the retort in an oil bath at 130° C., or a strong solution of calcium chloride may be used instead of oil.

Reaction:

$$3\ PCl_3 + KClO_3 = KCl + 3\ POCl_3.$$

The potassium chlorate must be perfectly dry or some potassium phosphate may be formed. The process requires about 4 hours. The yield should be about 530 gr. of pure oxychloride.

Properties:

Phosphorus oxychloride is decomposed by water, and is miscible with carbon disulphide without entering into combination. It has a disagreeable odor, and boils at 110° C.

65. PHOSPHORUS PENTACHLORIDE.*

PCl_5. M.W. = 208.5.

Take of

Phosphorus trichloride, 50 gr.

Arrange an apparatus as shown in Fig. XV. Through the rubber stopper of a wide-mouthed 100 cc. bottle, pass the inlet tube A, the outlet tube B, and the stem of a separating funnel C. The inlet tube is provided with a side branch, and has a stopper at its upper end, through which a glass rod passes, to be used in cleaning the tube should it become clogged. Fill the bottle with chlorine by connecting the side tube of A with the chlorine generator, and allow a few cc. of the trichloride to flow in from the funnel. Combination takes place at once, and a deposit of solid pentachloride is seen if the bottle be cooled by placing it in a vessel of cold water. Gradually introduce the trichloride in small portions; it combines with the chlorine, forming a solid mass. Repeat the process until the bottle is nearly filled.

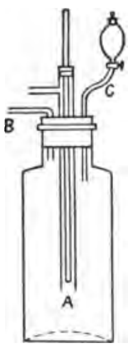

FIG. XV.

Properties:

Phosphorus pentachloride forms a yellowish white crystalline mass, volatile without melting, below 100° C. It has a disagreeable odor. It attracts moisture from the air and is decomposed, giving off hydrochloric acid. It is decomposed at once by water, forming oxychloride. It is used frequently in organic synthetical work.

* GATTERMANN, Praxis des organischen Chemikers.

66. PHOSPHORUS TRICHLORIDE.*

PCl_3. M.W. = 137.5.

Take of

Yellow phosphorus, 80 gr.

Break up the phosphorus under water in a porcelain mortar with a knife or chisel into lumps that will pass easily through the tubulature of a 400 cc. retort. Displace the air from the retort by passing into it a stream of carbon dioxide which has been dried by passing through sulphuric acid. Arrange the apparatus as in Fig.* XVI to connect with a chlorine generator. (See $AlCl_3$, p. 40.) Take each piece of phosphorus in a pair of forceps, and dry very quickly with several folds of filter paper. Transfer to the retort, taking care that it is not ignited by rubbing against the edge of the tubulature. Close the tubulature with a cork through which the delivery tube passes from the chlorine apparatus. Let the delivery tube fit loosely enough in the cork to permit its being adjusted to various depths in the retort. Fit the neck of the retort to a tubulated receiver (Fig. XVI, B) which may be cooled with water. An outlet pipe from the receiver to the hood or out of doors, must be provided to carry off excess of chlorine. Conduct a moderately rapid

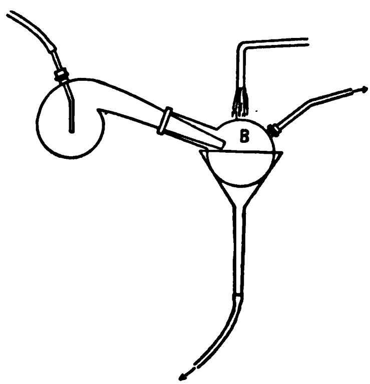

FIG. XVI.

* GATTERMANN, Praxis des organischen Chemikers, p. 244.

stream of chlorine through the retort. A tumultuous reaction between the phosphorus and chlorine begins; the phosphorus trichloride distills over into the receiver as a low boiling liquid.

If crystals of the pentachloride form in the neck of the retort, push the delivery tube for chlorine somewhat deeper into the retort. If introduced too far, however, a deposit of red phosphorus will form on the interior of the retort wall; in this case raise the tube slightly until this disappears. With a little care in adjusting the tube, the proper position at which the reaction best proceeds, is soon found.

Distill the phosphorus trichloride collected in the receiver, from a perfectly dry flask, by heating on the water bath. The yield is 250–280 gr.

Reaction:

$$P + 3\ Cl = PCl_3.$$

Properties:

Phosphorus trichloride is a colorless liquid, fuming in damp air and decomposed by water and by alcohol. It boils at 74° C. Frequent use is made of it in organic synthetical work. It has no action on ether, benzol, chloroform, nor carbon disulphide, and hence may be mixed with these substances.

67. POTASSIUM BICHROMATE.

$K_2Cr_2O_7$. M.W. = 295.

Take of

Chromite (powdered),	900	gr.
Potassium carbonate (free from chlorine),	450	"
Lime,	1400	"
Potassium sulphate,	150	"
Water,	4200	cc.

Dissolve the potassium carbonate in 500 cc. of water. Put the lumps of lime into a 12-inch evaporating dish, add about 300 cc. of the solution of carbonate, and let stand until the lime is slaked. Add the rest of the solution, stir well, and evaporate to dryness on the steam bath. Heat over a lamp to 150° C., and stir until thoroughly powdered. Add the powdered chromite, and mix very carefully. Ignite the mixture at a bright red heat for 3 or 4 hours in a muffle furnace, with free access of air, stirring very frequently. If a small reverberatory is at hand, it is better to heat it in this with an oxidizing flame. Cool the mass, pulverize coarse, and extract with 3000 cc. of water, stirring thoroughly. Concentrate the solution until crystals begin to form in it, and then add a hot concentrated solution of potassium sulphate, to precipitate the calcium from the calcium chromate. When no further precipitation takes place, filter off the calcium sulphate. To the yellow filtrate of potassium chromate, add sulphuric acid diluted with twice its volume of water until strongly acid, and let the liquid cool. If the solution of potassium chromate is nearly saturated, the addition of the acid, converting the chromate to bichromate, causes a precipitation of about two-thirds of the latter because of its greater insolubility. Filter off this crystalline precipitate on an asbestos or glass-wool

filter, using the suction pump. Redissolve the mass in hot water, and recrystallize, drain, and dry in the warming closet at a moderate temperature. The combined mother liquors may be evaporated further, but the resulting crystals are contaminated with potassium sulphate, from which it is very difficult to purify them.

Reactions:

$$2\ Cr_2FeO_4 + 4\ K_2CO_3 + 7\ O = 4\ K_2CrO_4 + Fe_2O_3 + 4\ CO_2.$$
$$2\ Cr_2FeO_4 + 4\ CaO + 7\ O = 4\ CaCrO_4 + Fe_2O_3.$$
$$CaCrO_4 + K_2SO_4 = K_2CrO_4 + CaSO_4.$$
$$2\ K_2CrO_4 + H_2SO_4 = K_2Cr_2O_7 + K_2SO_4 + H_2O.$$

The result of the ignition is the formation of potassium and calcium chromates in the mass, together with iron oxide and silicate of potassium. When lixiviated, the chromates go into solution. The addition of potassium sulphate decomposes the calcium chromate.

An excess of lime over the theoretical quantity is used, to keep the mass porous during ignition. Only about four-fifths of the theoretical amount of potassium carbonate is used, since the lime also combines with part of the chromium.

Properties:

Potassium bichromate crystallizes in orange-colored crystals without "water of crystallization." It melts somewhat below a red heat, and when heated higher decomposes, forming normal chromate, chromic oxide, and oxygen.

100 parts of water at

0° C.	dissolve	4.97	parts	$K_2Cr_2O_7$.*
10° "	"	8.5	"	"
20° "	"	13.1	"	"
40° "	"	29.1	"	"
60° "	"	50.5	"	"
80° "	"	73.0	"	"
100° "	"	102.0	"	"

* KREMERS, Pogg. Ann. **92**, 497.

The specific gravity of the aqueous solution at 19.5° C. containing

1%	K_2CrO_7	is 1.007.*
2%	"	" 1.015.
3%	"	" 1.022.
4%	"	" 1.030.
5%	"	" 1.037.
6%	"	" 1.043.
7%	"	" 1.050.
8%	"	" 1.056.
9%	"	" 1.065.
10%	"	" 1.073.
11%	"	" 1.080.
12%	"	" 1.085.
13%	"	" 1.097.
14%	"	" 1.102.
15%	"	" 1.110.

The commercial salt is usually very pure, containing only traces of chlorides and sulphates. It is largely used in making leather and in dyeing and coloring industries, and as a source of nearly all chromium compounds. It is a powerful oxidizing agent, and is used extensively in manufacturing operations for this purpose. Contact with organic matter causes a reduction of the bichromate on exposure to light, or on heating.

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68. POTASSIUM BINOXALATE.

KHC_2O_4. M.W. = 128.

Potassium Quadroxalate.

$KHC_2O_4 \cdot C_2H_2O_4 \cdot 2\,H_2O$. M.W. = 254.

The above salts are prepared in the same general way. By neutralizing one-half of the solution of oxalic acid, as directed

* GERLACH, Zeit. anal. Chem. **8**, 288.

in the preparation of the neutral oxalate on page 178, and adding the other half of the acid solution to the neutralized portion, the binoxalate crystallizes. For the quadroxalate, neutralize one-fourth of the oxalic acid solution with the potassium carbonate, and then add the remainder of the acid. Since the binoxalate and the quadroxalate are difficultly soluble, a precipitate forms in both cases. When entirely cold, decant the mother liquor, and drain and dry the crystals as directed on page 178 in the case of the neutral oxalate.

Properties:

Potassium binoxalate and potassium quadroxalate are acid salts which crystallize readily. The quadroxalate is soluble in 20 parts of water at 20° C. They are used to some extent in textile coloring and for removing ink and iron stains from cloth, also for cleaning metallic surfaces. They are sold in commerce under the name "salts of sorrel" or "lemon salts."

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69. POTASSIUM BROMATE.

$KBrO_3$. M.W. = 167.

Take of

Bromine,	435 gr.
Potassium hydrate,	305 "
Water,	500 cc.

Dissolve the caustic potash in the water in a 1200-cc. flask. Allow the bromine to drop rapidly from a separatory funnel into the caustic solution, while shaking the flask continually. Considerable heat is generated by the reaction, and it may be necessary to cool the flask somewhat under the tap, or by placing

it in cold water. Unless the caustic is very pure, the above quantity will not be sufficient to neutralize the bromine, and more must be added.* If there is an excess of bromine, the solution is yellow or red, and caustic should be added till the color disappears.

Cork the flask, and allow it to stand some hours in a cool place, and then filter off the precipitated bromate on the Büchner filter with suction. (See FILTRATION, p. 14.) The filtrate may be worked for potassium bromide (p. 163). The crystalline precipitate of bromate will probably be discolored by a precipitate of iron and aluminum hydrates from the caustic. If so, dissolve it in 500 cc. of boiling water, and filter on a hot-water funnel. (See FILTRATION, p. 13.) Let it stand over night in a cool place. Decant off the liquor, and suck the crystals as dry as possible by the filter pump. Evaporate the filtrate to one-third its bulk, and cool again to recover more of the bromate. Put the remaining mother liquor with the filtrate for bromide. Recrystallize the white crystals of potassium bromate from 350 cc. of distilled water, and repeat this operation if necessary.

The product should be about 135 gr. of clean crystals of bromate containing no more than a faint trace of bromide.

A solution of potassium carbonate may be used instead of caustic, but it must be heated in order to carry out the reaction and decompose the hypobromite and perbromide of potassium which have been formed.†

Reaction:

$$6\,KOH + 6\,Br = 5\,KBr + KBrO_3 + 3\,H_2O.$$

* In one trial the author found it necessary to add about 50 gr. excess of caustic over the theoretical amount, which indicated impurities to the extent of nearly 15%.

† BALARD, J. pr. Chem. 4, 165.

Properties:

Potassium bromate is not easily soluble in cold water, but is very soluble in hot water.

100 parts of water at

0°	C.	dissolve	3.11	parts	$KBrO_3$.*
20°	"	"	6.92	"	"
40°	"	"	13.24	"	"
60°	"	"	22.76	"	"
80°	"	"	33.90	"	"
100°	"	"	49.75	"	"

104° C. is the boiling point of a saturated solution.

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70. POTASSIUM BROMIDE.

KBr. • M.W. = 119.

(*a*) Take of

Sheet-iron strips,	50 gr.
Bromine,	133 "
Potassium carbonate C.P. dry,	115 gr.
Water,	1000 cc.

Into a 1500-cc. flask, put 1 liter of water and 100 gr. of bromine. Clean the iron strips by dipping into dilute hydrochloric acid until bright; then wash off the acid, and put two or three of the strips into the flask of bromine water. Allow it to stand at the ordinary temperature of the room, and soon the reaction begins. If it becomes very violent, cool the flask by standing it in cold water. The iron partly dissolves and when the solution (ferrous bromide) becomes a light green color, the bromine has all combined with the iron. It may be necessary to heat the flask on the water bath, or to allow it to stand over night to complete the reaction. Filter hot on a folded

* KREMERS, Pogg. **97**, 5.

filter to remove the residue derived from the iron, and add 33 gr. of bromine to the solution. The green color changes to a deep red brown. Heat to boiling to drive off any excess of bromine. Dilute with 2 liters of hot water, and pour into a deep beaker or dish of at least 5-liter capacity. Then add slowly, in small portions at a time, about 115 gr. of chemically pure, dry, potassium carbonate to the hot solution. A dense precipitate of ferroso-ferric hydrate falls, and carbon dioxide is set free, causing much effervescence and frothing. When a test filtered off gives no more precipitate on further addition of potassium carbonate, allow the solution to stand until the precipitate settles. Decant the clear liquor through a folded filter, and wash the precipitate twice with hot water by decantation (p. 20). Add the wash waters to the filtrate, evaporate to dryness, and heat to low red heat. Take up in hot water and concentrate the solution (potassium bromide) to a density of 75° Tw. (sp. gr. 1.375); filter off any precipitate of ferric hydrate which may have separated during the concentration, and allow to cool and crystallize.

The object of adding more bromine, is to convert the ferrous bromide into the ferroso-ferric state ; this gives a precipitate of ferroso-ferric hydrate that is much easier filtered off than the ordinary ferric hydrate.

Reactions:

$$Fe + Br_2 = FeBr_2.$$

$$3\ FeBr_2 + Br_2 = Fe_3Br_8.$$

$$Fe_3Br_8 + 4\ K_2CO_3 + 4\ H_2O = 8\ KBr + 4\ CO_2 + Fe_3(OH)_8$$

$$Fe_3(OH)_8 = [Fe(OH)_2 \cdot 2\ Fe(OH)_3].$$

(*b*) Potassium bromide may also be made in connection with the preparation of potassium bromate (p. 160). By treating caustic potash with bromine, 5 molecules of the bromide are

formed for each molecule of the bromate. The method of separating these salts is given on page 161. Evaporate the solution of potassium bromide obtained after crystallizing the bromate, to a thick solution, and stir 25 gr. of powdered charcoal into the mass. Evaporate to dryness, and ignite at a red heat, in small portions at a time, over a large lamp to decompose any bromate which may remain. Cool, and extract the grayish black mass with boiling water until a concentrated solution is obtained. Filter on a hot-water funnel (p. 13), and allow the solution to cool slowly. Extract the residue of charcoal once more with a little hot water, and add this filtrate to the other. Filter off the crystals of potassium bromide thus obtained, in the suction funnel, and evaporate the mother liquor for a second crop. Recrystallize once from distilled water. Dry in a desiccator over sulphuric acid.

Reactions:

$$6\ KOH + 3\ Br_2 = 5\ KBr + KBrO_3 + 3\ H_2O.$$
$$2\ KBrO_3 + 3\ C = 2\ KBr + 3\ CO_2.$$

The yield from 435 gr. of bromine is about 430 gr. of potassium bromide, after separating 135 gr. of bromate.

Properties:

Potassium bromide crystallizes in white cubes without "water of crystallization." It is somewhat soluble in dilute alcohol and very soluble in water.

100 parts of water at

0° C.	dissolve	53.48	parts	KBr.*
20° "	"	64.52	"	"
40° "	"	74.63	"	"
60° "	"	85.35	"	"
80° "	"	93.46	"	"
100° "	"	102.00	"	"

* KREMERS, Pogg. Ann. **97**, 151.

The specific gravity of solutions at 19° C. containing

5%	KBr	is	1.037.*
10%	"	"	1.075.
15%	"	"	1.116.
20%	"	"	1.159.
25%	"	"	1.207.
30%	"	"	1.256.
35%	"	"	1.309.
40%	"	"	1.366.
45%	"	"	1.432.

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71. POTASSIUM CHLORIDE.

KCl. M.W. = 74.5.

Take of

Crude potassium chloride,	1000 gr.
Water,	2500 cc.

The impurities present are sulphates and chlorides of sodium, calcium, and magnesium.

Dissolve the salt in the water at 80° C., and add some "milk of lime" to precipitate the magnesium, as in the preparation of sodium chloride (p. 195). Then add barium chloride to the hot solution until the sulphates are all precipitated, and filter. Precipitate the excess of lime and barium by adding ammonium carbonate, and filter again. Evaporate the filtrate to dryness, and heat to a low red heat until excess ammonium salt is removed. Add hydrochloric acid to the residue, dilute with distilled water, and boil well. Filter if not clear, concentrate to 41° Tw. (sp. gr. 1.205), and allow to crystallize. Dry the crystals as in the case of sodium chloride. Evaporate the mother liquor for more salt.

* GERLACH, Zeit. anal. Chem. 8, 285.

Usually from 25–30 gr. of anhydrous barium chloride are necessary to precipitate the sulphates present in this quantity of crude potassium chloride. Potassium carbonate may be used instead of ammonium carbonate to precipitate the lime and barium, but the precipitation may not be so complete.

Properties:

Potassium chloride is very soluble in water. 100 parts of water at

0°	C.	dissolve	28.5	parts	KCl.*
10°	"	"	32.0	"	"
20°	"	"	34.7	"	"
30°	"	"	37.4	"	"
40°	"	"	40.1	"	"
50°	"	"	42.8	"	"
60°	"	"	45.5	"	"
70°	"	"	48.3	"	"
80°	"	"	51.0	"	"
90°	"	"	53.8	"	"
100°	"	"	56.6	"	"
107°	"	"	58.5	"	"

The specific gravity of solutions at 17.5° C. containing

1%	KCl	is	1.0062.†
5%	"	"	1.0319.
10%	"	"	1.0655.
15%	"	"	1.1008.
16%	"	"	1.1080.
17%	"	"	1.1152.
18%	"	"	1.1225.
19%	"	"	1.1298.
20%	"	"	1.1372.
21%	"	"	1.1446.
22%	"	"	1.1521.
23%	"	"	1.1596.
24%	"	"	1.1673.

* MULDER, Scheik. Verhand. **1864**, 41.
† SCHIFF, Ann. **110**, 76.

72. POTASSIUM CHROMATE.

K_2CrO_4. M.W. = 194.5.

(*a*) Take of

Potassium bichromate,	500 gr.
Potassium carbonate (dry),	235 "
Water,	1500 cc.

Put the bichromate into a 14-inch evaporating dish, and add 1500 cc. of water. Heat on the steam bath to 80° C., and add the potassium carbonate in small portions at a time, stirring actively, waiting for the effervescence produced by each portion to cease before adding the next. The neutral chromate of potassium is very much more soluble than the bichromate, and it is only necessary to add water enough to dissolve the product of the reaction. The color of the solution changes from red to a clear yellow of considerable tinctorial strength.

After all the potassium carbonate has been added, heat the solution to boiling to drive off carbon dioxide, dilute it with 1 liter of water, and filter to remove any dirt. Evaporate the filtrate on the steam bath until a thick crust of crystals has formed on the bottom of the dish. Remove these, drain them free from adhering mother liquor, and dry at a low temperature, on a glass plate, in the drying closet; or the purified solution of neutral chromate may be carefully evaporated directly to dryness on the steam bath.

Reaction:

$$K_2Cr_2O_7 + K_2CO_3 = 2\ K_2CrO_4 + CO_2.$$

(*b*) From chromite. (See POTASSIUM BICHROMATE, p. 157.)

Properties:

Potassium chromate forms yellow prisms or plates without crystal water. It does not crystallize well, and is very difficult to purify by crystallization. It is very soluble. 100 parts of water at

0° C.	dissolve	58.90	parts	K_2CrO_4.*
10° "	"	60.92	"	"
20° "	"	62.94	"	"
30° "	"	64.96	"	"
40° "	"	66.98	"	"
50° "	"	69.00	"	"
60° "	"	71.02	"	"
70° "	"	73.04	"	"
80° "	"	75.06	"	"
90° "	"	77.08	"	"
100° "	"	79.10	"	"

The specific gravity of an aqueous solution at 19.5° C. containing

1%	of the salt	is	1.0080.†
5%	"	"	1.0408.
10%	"	"	1.0837.
15%	"	"	1.1287.
20%	"	"	1.1765.
25%	"	"	1.2274.
30%	"	"	1.2808.
35%	"	"	1.3386.
40%	"	"	1.3991.

With water, the crystals yield a clear solution which is very slightly alkaline to litmus. The usual impurities are sulphates, chlorides, and nitrates of the alkali metals. Commercial samples often contain excess of alkali.

Being difficult to purify and containing less chromic acid than the bichromate, potassium chromate finds but limited use in the arts and in the laboratory. It acts as an oxidizing agent.

* ALLUARD, Compt. Rend. **59**, 500.
† GERLACH, Zeit. anal. Chem. **8**, 288.

It is very poisonous; hence care must be exercised in handling it, especially if there be any cuts or scratches on the hands.

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73. POTASSIUM FERRICYANIDE.*

$K_3Fe(CN)_6$. M.W. = 329.

Take of

Potassium ferrocyanide,	200 gr.
Water,	300 cc.
Lead peroxide,	40 gr.

Dissolve the ferrocyanide in the water by heating in a 1200-cc. round-bottom flask. Pass a stream of carbon dioxide from a Kipp's apparatus into the solution while raising to boiling. Then add 20 gr. of the lead peroxide to the hot solution, and let it boil for an hour or more, while passing a strong stream of carbon dioxide † into it.

If the precipitated lead carbonate in the flask causes much bumping, which might break the flask, filter hot on a Büchner filter (p. 14), add a fresh portion of 20 gr. of lead peroxide to the filtrate, and boil again while passing the carbon dioxide into it. As the lead carbonate continues to be precipitated and the bumping again becomes violent, it may be necessary to repeat this process several times, until the filtrate gives no precipitate when tested with a solution of ferric chloride. Then put the hot solution of potassium ferricyanide into a covered beaker, and let it cool very slowly.

* Lunge, Ding. J. **238**, 75; also Jahresb. **1880**, 387. Seuberlich, Ding. J. **238**, 482.

† An excess of carbon dioxide must be present to prevent the decomposition of the ferricyanide by the PbO and KOH formed in the reaction.

Pour off the liquor from any crystals which may have formed, and concentrate on the water bath until small crystals begin to separate on the surface of the liquid. Add a very few cc. of hot distilled water to redissolve these, and filter hot, to remove the brown precipitate which has separated during the concentration. Let it stand over night in the covered beaker to crystallize as before. Drain the combined crystal products, and dry them in a desiccator over calcium chloride or sulphuric acid. Concentrate the mother liquor further for more crystals.

Should crystals of ferrocyanide begin to deposit, as yellow plates, along with the red crystals of ferricyanide, treat the solution again with lead peroxide and carbon dioxide.

After three or four crops of crystals, the mother liquor becomes so contaminated with bicarbonate of potassium and other impurities, that it will not yield clean crystals; in this event, recrystallize the product from a small amount of distilled water. The amount of pure ferricyanide obtained from the above quantity of ferrocyanide should be about 135 gr., or, approximately, 75% of the theoretical yield.

Reaction:

$$2\ K_4Fe(CN)_6 + PbO_2 + 2\ CO_2 + H_2O = 2\ KHCO_3 + PbO + 2\ K_3Fe(CN)_6.$$

Properties:

Potassium ferricyanide crystallizes in slender, blood-red crystals, which dissolve freely in water, forming a greenish yellow solution. The salt is known in commerce as "red prussiate of potash." Its use in qualitative analysis is well known. Its solution is unstable and should be prepared as needed, by dissolving a small crystal of the salt.

100 parts of water at

4.4° C.	dissolve	33.	parts	of the	salt.*
10. ° "	"	36.6	"	"	"
15.6° "	"	40.8	"	"	"
37.8° "	"	58.8	"	"	"
100. ° "	"	77.5	"	"	"
104.5° "	"	82.6	"	"	"

The specific gravity of solutions at 13° C. containing

1%	of the	salt is	1.0051.†
5%	"	"	1.0261.
10%	"	"	1.0538.
15%	"	"	1.0831.
20%	"	"	1.1039.
25%	"	"	1.1462.
30%	"	"	1.1802.

Potassium ferricyanide may also be prepared by treating a hot concentrated solution of ferrocyanide with bromine, according to the proportions required in the following equation:

$$K_4Fe(CN)_6 + Br = KBr + K_3Fe(CN)_6.$$

But any excess of bromine results in the formation of a dirty green precipitate, which passes through any filter and contaminates the product, and it is difficult to remove the bromide formed, from the ferricyanide. For these reasons the author has found the preceding process much more satisfactory as a laboratory method.

* Wallace, J. Chem. Soc. **7**, 80.
† Schiff, Ann. **113**, 350.

74. POTASSIUM IODIDE.

KI. M.W. = 166.

(*a*) Take of

Iron (nails or band),	75 gr.
Iodine,	250 "
Water,	400 cc.
Potassium carbonate, C. P.,	135 gr.

Treat the iron with acid until bright and clean, and wash it thoroughly with hot water. Put it into a 1000-cc. flask, and add 200 cc. of water, and then 190 gr. of the iodine in small portions at a time, while warming the flask on the water bath. Shake the flask after each addition of the iodine. The liquid becomes reddish brown in color, and soon considerable heat is developed. Remove from the water bath, and let the flask stand for several hours, shaking it at frequent intervals, and then let it stand quietly over night. Heat for an hour on the water bath, and bring to boiling on the sand bath and boil ten minutes. Filter boiling hot, on a folded paper filter, catching the filtrate in another flask. The solution (ferrous iodide) should now be a clear green color and give no blue coloration when tested with iodo-starch solution. To this green liquid add the remaining 60 gr. of iodine, and heat to boiling for a few minutes. Vapor of iodine may escape during the boiling. The ferrous iodide is converted to ferroso-ferric iodide, and becomes deep red brown in color. Pour this solution into 3 liters of hot water in a 14-inch evaporating dish, and heat to boiling. Meanwhile dissolve the 135 gr. of potassium carbonate in 200 cc. of hot water, and add this solution, a few cc. at a time, to the *hot* solution of ferroso-ferric iodide, while stirring actively. A dense, brownish black precipitate of ferroso-ferric hydrate falls, and large quantities of carbon dioxide escape, causing the solution to froth considerably. When

175 cc. of the carbonate solution have been added, filter off 10 cc. of the mixture in the dish, and add another drop of the carbonate solution to the filtrate; if a precipitate of iron hydrate falls, add another 10 cc. of the carbonate solution to the contents of the dish, stir well, and repeat the test. When all the iron has been precipitated, allow the dish to stand quietly for a short time, and the precipitate will settle rapidly, leaving the supernatant liquor (potassium iodide) very clear. Decant through a folded filter, or filter it through a Büchner funnel, using suction (p. 14). Finally bring the precipitate into the funnel, and drain off as much of the liquid as possible; return the precipitate to the dish, wash two or three times with hot water, and add the filtered wash waters to the solution of potassium iodide. Evaporate rapidly over the lamp until nearly saturated. If a precipitate of ferric hydrate separates during evaporation, it must be filtered off before allowing the solution to cool; or the entire solution may be evaporated to hard dryness, and then on extracting with hot water, the iron is left as insoluble matter.

The mass of iron hydrate obtained should be washed with hot water till free from iodide, and used for the preparation of iron chloride (p. 107).

Care must be taken to add but a slight excess of potassium carbonate in neutralizing; otherwise the product is certain to be contaminated with carbonate. The carbonate used should be chemically pure, to avoid the introduction of sulphate or chloride into the product, and thoroughly dry, to secure accuracy in the amount taken.

Reactions:

$$Fe + I_2 = FeI_2.$$
$$3\,FeI_2 + I_2 = Fe_3I_8.$$
$$Fe_3I_8 + 4\,K_2CO_3 + 4\,H_2O = 8\,KI + 4\,CO_2 + Fe_3(OH)_8.$$

(*b*) Potassium iodide may also be prepared by dissolving 100 gr. of iodine in a solution of 45 gr. of pure caustic potash in 250 cc.

of water. Concentrate this solution to a thick syrup, add 5 gr. of powdered charcoal, and evaporate to hard dryness. Ignite at a red heat, in a porcelain or iron crucible. Extract with hot water, filter, evaporate the filtrate to saturation, and allow to crystallize.

Reactions :

$$3\,I_2 + 6\,KOH = 5\,KI + KIO_3 + 3\,H_2O.$$
$$2\,KIO_3 + 3\,C = 2\,KI + 3\,CO_2.$$

Method (*a*) gives a product free from iodate and is generally preferred for the preparation of a pure salt.

Properties :

Potassium iodide forms white cubical crystals, of a sharp, salty taste. It is very soluble in water and slightly so in alcohol.

100 parts of water at

0°	C. dissolve	127.9	parts	KI.*	65°	C. dissolve	180.	parts	KI.
5°	" "	132.1	"	"	70°	" "	184.	"	"
10°	" "	136.1	"	"	75°	" "	188.	"	"
15°	" "	140.2	"	"	80°	" "	192.	"	"
20°	" "	144.2	"	"	85°	" "	197.	"	"
25°	" "	148.3	"	"	90°	" "	201.	"	"
30°	" "	152.3	"	"	95°	" "	205.	"	"
35°	" "	156.0	"	"	100°	" "	209.	"	"
40°	" "	160.	"	"	105°	" "	213.	"	"
45°	" "	164.	"	"	110°	" "	218.	"	"
50°	" "	168.	"	"	115°	" "	222.	"	"
55°	" "	172.	"	"	117°	" "	223.6	"	"
60°	" "	176.	"	"					

The specific gravity of solutions at 21° C. containing

1%	KI is	1.0075.†	35%	KI is	1.3389.
5%	"	1.0384.	40%	"	1.4079.
10%	"	1.0793.	45%	"	1.4825.
15%	"	1.1226.	50%	"	1.5640.
20%	"	1.1705.	55%	"	1.6528.
25%	"	1.2229.	60%	"	1.7517.
30%	"	1.2784.			

* Mulder, Scheik. Verhand. **1864**, 63.

† Schiff, Ann. **110**, 75.

The aqueous solution dissolves free iodine very readily, forming a solution of potassium triiodide (KI_3) which is easily decomposed.

On long standing, especially if exposed to light, potassium iodide decomposes somewhat and becomes yellowish in color. When crystallized from a slightly alkaline solution it keeps better than a perfectly neutral salt.

It is extensively used in medicine and in photography. The crystals should give no tests for chlorides, sulphates, or nitrates, and the aqueous solution should not alter when hydrogen sulphide is passed into it. The dilute solution prepared with distilled water which has been recently boiled and cooled, should give no blue color when mixed with dilute, pure sulphuric acid and iodo-starch solution.

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75. POTASSIUM NITRATE.

(Saltpetre.)

KNO_3. M.W. = 101.

(*a*) Take of

Potassium chloride (purified),	3000 gr.
Sodium nitrate (purified),	3425 "
Water,	6000 cc.

Mix the dry salts in a weighed crock, add 3 liters of hot water, and dissolve the salts by blowing in free steam, until the condensed steam brings the weight of the water in the crock to 6 kilos, and the temperature is not lower than 90° C. Stir well at frequent intervals while passing in the steam. Then transfer to a 16-inch evaporating dish, and heat to boiling, stirring actively to prevent the precipitated sodium chloride from settling to the bottom of the dish. Filter boiling hot on

a cloth bag filter (p. 14), and evaporate the filtrate to about 4 liters. If any salt separates during this evaporation, filter boiling hot, a second time. Allow to cool several hours, and pour off the mother liquor, from the crystals of potassium nitrate. The residues of sodium chloride obtained by the first filtrations should be stirred up with this mother liquor and heated to boiling. Filter hot, concentrate the filtrate to about half its volume, and cool slowly. More potassium nitrate crystallizes. This mother liquor may be thrown away, as it is not worth further concentration.

Dissolve the combined products of potassium nitrate in 2 liters of distilled water, and recrystallize several times to free from adhering sodium chloride. Dry the crystals in the hot closet after draining thoroughly.

Reaction:

$$KCl + NaNO_3 = KNO_3 + NaCl.$$

(*b*) Potassium nitrate may be obtained very pure as a by-product in the preparation of lead chromate (p. 121). Draw off the liquid in which the precipitation of lead chromate has been made, and concentrate to about 4 liters. Test for the presence of lead by adding a drop of neutral potassium chromate solution. If a precipitate forms, add more chromate until all of the lead is thrown down, but avoid any excess of potassium chromate. Filter, evaporate the filtrate until concentrated, and allow to cool slowly. The potassium nitrate crystallizes nearly pure, but should be recrystallized from distilled water.

Properties:

Potassium nitrate crystallizes in long prisms or needles without "water of crystallization." Its solubility increases very rapidly as the temperature increases.

100 parts of water at

0° C.	dissolve	13.3	parts of the salt.*
10° "	"	21.1	" " "
20° "	"	31.2	" " "
25° "	"	37.3	" " "
30° "	"	44.5	" " "
40° "	"	64.0	" " "
50° "	"	86.	" " "
60° "	"	111.	" " "
70° "	"	139.	" " "
80° "	"	172.	" " "
85° "	"	189.	" " "
90° "	"	206.	" " "
95° "	"	226.	" " "
100° "	"	247.	" " "
105° "	"	272.	" " "
110° "	"	301.	" " "
114° "	"	326.	" " "

The specific gravity of aqueous solutions at 15° C. containing

1%	potassium	nitrate is	1.00641.†
2%	"	"	1.01283.
3%	"	"	1.01924.
4%	"	"	1.02566.
5%	"	"	1.03207.
6%	"	"	1.03870.
7%	"	"	1.04534.
8%	"	"	1.05197.
9%	"	"	1.05861.
10%	"	"	1.06524.
11%	"	"	1.07215.
12%	"	"	1.07905.
13%	"	"	1.08596.
14%	"	"	1.09286.
15%	"	"	1.09977.
16%	"	"	1.10701.
17%	"	"	1.11426.
18%	"	"	1.12150.
19%	"	"	1.12875.
20%	"	"	1.13599.
21%	"	"	1.14361.

* MULDER, Scheik. Verhand. **1864**, 89. † GERLACH, Zeit. anal. Chem. **8**, 286.

Potassium nitrate is a powerful oxidizing substance, and finds frequent use as such in the laboratory. The commercial salt is known as saltpetre, and usually contains more or less chloride and sulphate and traces of lime and magnesia.

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76. POTASSIUM OXALATE.

$K_2C_2O_4 \cdot 2\ H_2O$. M.W. = 202.

Take of

Oxalic acid (purified),	1000 gr.
Potassium carbonate (dry),	1095 "
Water,	2000 cc.

Put the oxalic acid into a 12-inch evaporating dish, add a liter of boiling water, and stir until all dissolved. Dissolve the potassium carbonate in a liter of hot water, and add this solution to the hot acid solution, slowly, in small portions at a time. The action is violent at first, and care must be taken lest spattering occur. A precipitate of the acid oxalate soon begins to form, but redissolves on the addition of sufficient carbonate. When the evolution of carbon dioxide becomes slow at each fresh addition of the carbonate, heat the solution to boiling, and put a small piece of litmus paper one-fourth of an inch square, into the dish to show when the liquid is alkaline. The exact amount of carbonate necessary can thus be ascertained, and no excess should be added.

Filter the hot solution of potassium oxalate, and allow it to crystallize. More crystals may be obtained by further evaporation of the mother liquor. Drain them in a covered funnel.

Reaction:

$$H_2C_2O_4 \cdot 2\, H_2O + K_2CO_3 = K_2C_2O_4 \cdot 2\, H_2O + CO_2 + H_2O.$$

Properties:

Potassium oxalate forms transparent or white crystals, having 2 molecules of crystal water. It is easily soluble, dissolving in 3 parts of water at 16° C.

It is used somewhat in photography and to a small extent in analytical work.

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77. POTASSIUM PERMANGANATE.*

$KMnO_4$. M.W. = 158.

Take of

Caustic potash,	210 gr.
Chlorate of potassium,	105 "
Pyrolusite (powdered and ignited),	180 "
Water,	300 cc.

Ignite the powdered pyrolusite at a red heat on an iron plate, to burn out any carbonaceous matter it may contain. Dissolve the caustic in the water, in an 8-inch evaporating dish, stir in the chlorate of potassium, and heat until dissolved. Then stir in the pyrolusite, and evaporate over the lamp to a smooth, thick paste. Heat this paste to redness over the lamp, in a loosely covered iron crucible or dish, in portions of about 100 cc. at a time, as the mass is liable to swell some on heating. The paste soon solidifies to a dark green or brown mass (potassium manganate), and vapor of water escapes. When thoroughly hard, let the crucible cool, and break out

* BRADBURY, Chem. Centralb. **1891**, 570. GREGORY, J. Pharm. **21**, 312.

the mass with an old chisel or other sharp-pointed tool. Then pulverize it, and boil in a large excess (4 liters) of water, passing a stream of carbon dioxide into the boiling solution for an hour, to convert the potassium hydrate to carbonate. The green liquid passes over into a violet solution of potassium permanganate, and a dense brown precipitate forms. Allow the whole to stand quietly for some time, and the precipitate settles to the bottom. Decant through an asbestos or glass-wool filter (p. 12), and finally bring the mud on the filter, and drain with suction. Return the mud to the beaker, and wash once or twice with a small amount of hot water, by decantation (p. 20), pouring the wash waters through the filter, and combine the filtrates. Evaporate rapidly over the lamp, until needle-like crystals appear on the surface of the liquid, and allow it to cool in a place well protected from dust. Pour off the mother liquor from the crystals, and evaporate further, after adding a little dilute hydrochloric or sulphuric acid to neutralize some of the excess of potassium carbonate in the solution. This second crop of crystals will be contaminated with sulphate or chloride of potassium, and should be recrystallized from distilled water.

Drain the crystals by suction, and dry in a desiccator over sulphuric acid.

Throughout the entire process, care must be taken that no organic matter comes in contact with the preparation, as the permanganate is readily reduced.

Reactions:

$$6\,MnO_2 + 2\,KClO_3 + 12\,KOH = 6\,K_2MnO_4 + 2\,KCl + 6\,H_2O.$$

$$3\,K_2MnO_4 + 6\,H_2O = 2\,KMnO_4 + 4\,KOH + MnO_2 + 4\,H_2O.$$

Properties:

Potassium permanganate is soluble in 16 parts of water at 15° C. The dilute solution is neutral, and when boiled with a little alcohol, should give a colorless filtrate containing no traces of sulphates nor chlorides. Neither should the solution, after decolorization with oxalic acid, give any test for nitrate with sulphuric acid and ferrous sulphate.

Potassium permanganate is a powerful oxidizing material, and it is frequently employed in laboratory experiments for this purpose. Its use as an analytical reagent in volumetric analysis is also very general.

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78. POTASSIUM-SODIUM TARTRATE.

(Rochelle Salts.)

$KNaC_4H_4O_6 \cdot 4\ H_2O$. M.W. = 282.

Take of

Sodium carbonate, C. P., dry,	142 gr.
Cream of tartar ($KHC_4H_4O_6$),	500 "
Water,	1200 cc.

Dissolve the sodium carbonate in the water, in a 14-inch evaporating dish, and heat to boiling. Pulverize the cream of tartar, and add it to the boiling solution in small portions at a time, allowing each portion to dissolve completely before adding the next. A vigorous effervescence takes place, and considerable frothing may occur. When all the cream of tartar has been dissolved in the solution, the liquid should show a slight alkaline reaction; if not, add a few drops of a strong solution of sodium carbonate until alkaline. Filter hot,

and allow it to stand quietly for a day to crystallize. Pour off the mother liquor, evaporate it about one-half, and allow to crystallize. Drain the large, transparent crystals in a funnel, and dry on a glass plate in the open air. They should be perfectly dry before bottling.

Cream of tartar is difficultly soluble in water, but Rochelle salt is very soluble; hence it is only necessary to use enough water to keep the product in solution, if the cream of tartar be *added to the carbonate solution*, and in small quantities at a time.

Reaction:

$$2\ KHC_4H_4O_6 + Na_2CO_3 + 3\ H_2O = 2\ KNaH_4C_4O_6 + 4\ H_2O + CO_2.$$

Properties:

Rochelle salt (also called Seignette * salts) forms large rhombic prisms, which dissolve in 1.7 parts of cold water and in much less when hot. The salt is used in the preparation of Fehling's solution for sugar analysis, and for some other purposes in the laboratory; also in medicine.

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79. SILVER NITRATE.

$AgNO_3$. M.W. = 170.

(*a*) From silver:

Take of

Silver (coin or scraps),	50 gr.
Nitric acid, C. P., 67° Tw. (sp. gr. 1.335),	65 cc.
Water,	40 "

* From its discoverer, SEIGNETTE (1672).

Put the silver into a 6-inch evaporating dish, and pour over it 30 cc. of the nitric acid which has been diluted * with an equal volume of water. If the reaction does not start spontaneously, warm the dish gently until it begins. When it becomes quiet, add the remaining 35 cc. of acid diluted with one-third of its volume of water. Finally heat the dish until all the metal is dissolved, and evaporate to dryness over the lamp, being very careful at the last to heat very gently to avoid spattering. When dry, raise the temperature to about 250° C. to decompose any copper nitrate which may have formed in the solution from the copper alloy in the silver. The mass becomes dark-colored and melts to a thick liquid. The copper nitrate decomposes to form copper oxide, but the silver nitrate is unchanged. Allow to cool, and extract the mass with 50 cc. of hot water, filter on glass wool (p. 12), and evaporate the solution to small bulk (about 25 cc.), and allow to cool in a desiccator over sulphuric acid. Evaporate the mother liquor, and if free from copper, the residue may be put with the other crystals. Dry the crystals in the desiccator over sulphuric acid.

During the entire process of purification and crystallization, care must be taken to protect the silver nitrate from dust or organic matter, and from fumes of hydrogen sulphide or hydrochloric acid. Otherwise the crystals become dark-colored when exposed to the light. The preparation should not be attempted in a room where the atmosphere is not pure. The crystals will turn black if touched with the bare hand.

Reaction:

$$6\ Ag + 8\ HNO_3 = 6\ AgNO_3 + 2\ NO + 4\ H_2O.$$

(*b*) From silver residues:

Take the residues which collect in the laboratory, evaporate

* The acid must be diluted because metallic silver is very slightly soluble in concentrated nitric acid, even when hot.

to dryness, treat with an excess of common hydrochloric acid, and again evaporate to dryness. Wash with boiling water until free from soluble chlorides and sulphates, and dry thoroughly in an evaporating dish on the steam bath. Mix the dry residue with 4 times its weight of a mixture of equal parts of sodium and potassium carbonates, and fuse the mass in a clay crucible at a red heat. When in quiet fusion, stir with an iron rod, giving the contents of the crucible a rotary motion. Pour into an iron mould to cool. Remove the adhering fused carbonate from the button of metallic silver which has collected in the point of the mould. Boil the silver with water containing a little hydrochloric acid to remove all traces of carbonates. Then treat the metallic silver as described in (*a*).

Instead of fusing the silver nitrate, the copper may be precipitated from the solution by boiling it with silver oxide, which may be obtained by adding caustic soda to about one-sixth of the silver nitrate solution. Wash the precipitate, which contains copper and silver oxides, with hot water until free from sodium salts, and add it to the silver nitrate solution. By this means the remaining copper is precipitated as oxide, and a corresponding part of the silver oxide is redissolved. Filter the solution hot, and evaporate to crystallize as in (*a*).

Properties:

Silver nitrate forms white plates or scales without "water of crystallization." It dissolves very readily in water, forming a colorless solution which does not react with litmus.

100 parts of water at

0° C.	dissolve	121.9	parts	of the	salt.*
19.5° "	"	227.3	"	"	"
54° "	"	500.	"	"	"
85° "	"	714.	"	"	"
110° "	"	1111.	"	"	"

* KREMERS, Pogg. Ann. **92**, 497.

It is very slightly soluble in concentrated nitric acid, and also dissolves in dilute alcohol. It fuses unchanged at 225° C., but on heating to a red heat more or less decomposition occurs.

The fused nitrate solidifies to a white, crystalline mass. It has a very corrosive action on organic matter, and becomes black on exposure to light, if organic matter is in contact with it.

It is extensively used in medicine, in photography, and is an important laboratory reagent. It should dissolve in distilled water, forming a perfectly clear solution containing no more than minute traces of other metals.

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80. SODIUM ACETATE.*

$NaC_2H_3O_2 \cdot 3\,H_2O$. M.W. = 136.

Take of

Sal soda,	2000 gr.
Acetic acid (common No. 8), (sp. gr. 1.04),	2900 cc.

Since this commercial acetic acid contains about 30% $C_2H_4O_2$, 2900 cc. are needed. Dissolve the sal soda in about 900 cc. of water, in a 16-inch evaporating dish and pour in the acid very slowly, with constant stirring. When nearly all the acid has been added, heat to boiling for a short time, test the solution with litmus paper, and continue adding acid until the liquid is acidified. Filter the solution if it is not clear, evaporate to crystallize, and dry the crystals thoroughly in the warm closet.

* J. W. Smith, private communication.

Then melt them in an agateware or iron pan, heating over free flame, with continual stirring, until all the water is expelled. This fusion decomposes the empyreumatic matters derived from the acetic acid. It is best to put only a few lumps of the dry mass into the pan at first, fusing them, and adding the remainder a little at a time.

Keep the mass in a fused condition, at about 300° C. for half an hour, controlling the temperature by the use of a thermometer. Now pour the melted acetate into a clean, cold iron plate, or into a broken evaporating dish to solidify. When cold, it should be of a silvery gray color and crystalline structure.

The fused acetate thus prepared may be used directly for various organic preparations, such as acetic anhydride, etc., when an anhydrous acetate is necessary.

For pure crystallized acetate, dissolve the fused mass in about 900 cc. of hot distilled water, and filter to remove the sediment of carbon and iron. Evaporate to 36° Tw. (sp. gr. 1.180), and crystallize. The mother liquor should be further concentrated, filtered, and recrystallized. After draining the crystals, dry them on a glass plate in the *coolest* part of the drying closet. (See DRYING, p. 26.)

Caution. — In the above fusion the temperature must not exceed 310° C., or decomposition of the sodium acetate may result. It is also necessary to exercise much care in adding fresh lumps to the fused mass that no wet piece, or water, drops into the fusion, as this would cause spattering. The hand should be protected by being wrapped in a towel while stirring.

Reaction:

$$Na_2CO_3 \cdot 10\ H_2O + 2\ C_2H_4O_2 = 2\ Na(C_2H_3O_2) \cdot 3\ H_2O + CO_2 + 5\ H_2O.$$

Properties:

Sodium acetate dissolves in 2.8 parts of water at 15° C. and in 0.5 parts of water at 100° C. The crystallized salt melts in its water of crystallization at 58° C. and loses all water at 130° C. The crystals effloresce when exposed to the air, and ultimately lose all their crystal water.

The specific gravity of a solution at 12.5° C. containing

5%	$NaH_3C_2O_2$	is	1.0146	sp. gr.
10%	"	"	1.0299	" "
20%	"	"	1.0619	" "
30%	"	"	1.0955	" "
50%	"	"	1.1755	" "

Commercial sodium acetate is often made by adding sodium sulphate solution to calcium or lead acetate solution, filtering off the precipitate, and evaporating the liquid. The preparation should be free from *iron* or *calcium* and from *chlorides*, *carbonates*, and *sulphates*. The aqueous solution of sodium acetate should be alkaline to litmus.

It is used in dyeing and coloring; also in medicine, and for many purposes in the arts.

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81. SODIUM BICARBONATE.

$NaHCO_3$. M.W. = 84.

Take of

Ammonia (sp. gr. 0.910),	250 cc.
Common salt,	220 gr.
Water,	2000 cc.

Put the concentrated ammonia into a 2000-cc. flask, add 1 liter of water, and pass into it a steady stream of carbon dioxide

from a Kipp's generator (see EXPERIMENT, p. 55), as long as the gas absorbs. Keep the flask cool during absorption, by running cold water over it constantly. If a precipitate forms during this carbonation, add a little more water until it just dissolves.

Dissolve the salt in 700 cc. of water at 15° C., forming a saturated solution, and add to it the ammonium bicarbonate solution as long as a precipitate falls. Keep the solutions cold during the precipitation. When no more sodium bicarbonate precipitates, filter on a Büchner filter with suction (p. 14). Wash the bicarbonate with a small amount of cold water to remove the adhering ammonium chloride solution. Dry the mass in the warm closet.

The yield will vary somewhat according to the temperature and concentration of the solutions. A considerable part of the salt used will unavoidably be lost, owing to the solubility of sodium bicarbonate in ammonium chloride solutions.

Reactions:

$$NH_3 + H_2O + CO_2 = NH_4HCO_3.$$
$$NH_4HCO_3 + NaCl = NaHCO_3 + NH_4Cl.$$

This preparation illustrates the principles on which the Solvey or Ammonia Soda Process depends. In the technical production of soda by this process, however, the order of the operations is slightly different from that given above. A concentrated brine solution is saturated with ammonia gas, and carbon dioxide is forced into this ammoniacal brine, causing the bicarbonate of soda to precipitate.

Properties:

Bicarbonate of soda is much less soluble in water than the neutral carbonate.

100 parts of water at

0° C.	dissolve	6.90	parts	$NaHCO_3$.*
5° "	"	7.45	"	"
10° "	"	8.15	"	"
15° "	"	8.85	"	"
20° "	"	9.60	"	"
25° "	"	10.35	"	"
30° "	"	11.10	"	"
35° "	"	11.90	"	"
40° "	"	12.70	"	"
45° "	"	13.55	"	"
50° "	"	14.45	"	"
55° "	"	15.40	"	"
60° "	"	16.40	"	"

The aqueous solution is alkaline. It separates from solution as a crystalline precipitate, containing no "water of crystallization." When ignited the dry salt gives off carbon dioxide and water, and passes over to the neutral carbonate, yielding a very pure soda. (See C. P. CARBONATE, p. 192.)

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82. SODIUM BROMIDE.

NaBr. M.W. = 103.

Sodium bromide may be made in the same way as potassium bromide (p. 162), by decomposing a solution of iron bromide with sodium carbonate, by boiling them together. Or bromine may be allowed to drop into a solution of caustic soda or of carbonate of soda (p. 163), and if the resulting mixture of bromide and bromate of sodium, obtained by evaporating the solution, is ignited, the bromate is converted to bromide.

* DIBBITS, J. pr. Chem. [2] **10**, 417.

Reactions:

$$Fe_3Br_8 + 4\ Na_2CO_3 + 4\ H_2O = 8\ NaBr + 4\ CO_2 + Fe_3(OH)_8.$$
$$6\ NaOH + 6\ Br = 5\ NaBr + NaBrO_3 + 3\ H_2O.$$

Properties:

Sodium bromide is very soluble. 100 parts of water at

0° C.	dissolve	77.5	parts of NaBr.*
20° "	"	88.4	" " "
40° "	"	104.2	" " "
60° "	"	111.1	" " "
80° "	"	112.4	" " "
100° "	"	114.9	" " "

The specific gravity at 15° C. of a solution containing

5%	NaBr	is	1.040.†
10%	"	"	1.080.
20%	"	"	1.174.
30%	"	"	1.281.
40%	"	"	1.410.
50%	"	"	1.565.

When crystallized from aqueous solution above 30° C., the crystals contain no "water of crystallization," but when crystallized below this point, they contain 2 H_2O. The anhydrous salt forms cubical crystals, and the hydrated variety is monoclinic.

The hydrated salt melts at 50° C. and becomes anhydrous.

* KREMERS, Pogg. Ann. **97**, 14.
† GERLACH, Zeit. anal. Chem. **8**, 285.

83. SODIUM CARBONATE.

Na_2CO_3. M.W. = 106.

$Na_2CO_3 \cdot 10\ H_2O$ (sal soda). M.W. = 286.

Take of

Soda ash,	2000 gr.
Water,	4500 cc.

(*a*) Dissolve the soda ash in the water, by heating to about 80° C. If the dry soda ash be placed in a dish and water poured over it, the entire mass is liable to cake together in a solid lump, whose solution then becomes very slow and difficult. To avoid this, it is better to pour the pulverized soda ash, into the hot water in a fine stream, while stirring actively; or to put the soda ash into a crock, and blow free steam into it until it is dissolved. When solution is completed, filter off the insoluble matter on a cloth filter, evaporate the filtrate to 47° Tw. (sp. gr. 1.235), and allow it to cool slowly to 10–12° C. Large crystals of *sal soda*, $Na_2CO_3 \cdot 10\ H_2O$, are formed. Pour off the mother liquor, and evaporate it further for more crystals. Remove the crystals from the dish, break up all large lumps, and put the whole mass through the centrifugal machine, until no more liquor can be separated. The crystals should feel dry to the hand. Spread them on a dry glass plate, and allow them to dry in the air until the edges begin to turn white. Then put them into a dry bottle immediately, and stopper tightly. If the solution of soda ash, is yellow or brown, a small amount of bleaching powder may be put in, to decolorize it. Filter off the precipitate before concentrating the solution to crystallize it.

Traces of chlorides and sulphates, which usually contaminate soda ash, are not removed by this process of making sal soda, but may remain after several recrystallizations; and traces of

silica may be present, dissolved from the porcelain and glass vessels used in its preparation.

(*b*) To prepare a salt free from chloride and sulphate, use the commercial bicarbonate as material. Put 600 gr. of bicarbonate into a large funnel whose neck is plugged with cotton, level off the upper surface of the salt, and cover with a circular piece of filter paper, laid on the salt. Pour small quantities of distilled water (25–30 cc.) on this paper from time to time, and let it percolate through the soda. After 400 cc. of water have been used for this washing, test the filtrate as it runs from the funnel, for chloride and sulphate. When, after acidifying the filtrate with nitric acid, no turbidity is produced by either silver nitrate or barium chloride, the washing is finished. Dry the remaining bicarbonate by suction and in the hot closet, and finally ignite at a low red heat in a platinum, silver, or porcelain dish. Dissolve the ignited mass in warm water, filter if necessary, and evaporate to crystallize.* This should yield a sal soda, pure except for traces of silica.

(*c*) According to J. Lawrence Smith,† a pure sodium carbonate may be prepared by precipitating a cold, solution of 145 gr. of sal soda in 100 cc. of water with a solution of 60 gr. of pure oxalic acid dissolved in 100 cc. of warm water. Put the sodium oxalate which separates into a 6-inch funnel, and wash with 500 cc. of distilled water as above described, using the filter pump (p. 13). Then dry, and heat to full redness in a platinum dish until the oxalate is decomposed. Dissolve, filter, and recrystallize.

Properties:

Sal soda forms large colorless crystals containing 10 molecules of water. At 34° C. these crystals melt in their "water

* Fresenius.

† Fresenius, Manual of Qual. Chem. Anal., 12th ed., p. 79.

of crystallization." On exposure to the air they soon effloresce and fall to a white powder having the composition $Na_2CO_3 \cdot H_2O$.

Anhydrous sodium carbonate, obtained by igniting the hydrated crystals, is a pure white powder which should dissolve in water without turbidity or leaving any residue. If not carefully prepared it may contain some caustic soda. It melts at a red heat with slight decomposition. On exposure to the air it absorbs moisture which may amount to from 6–8% of the total weight.

Pure sodium carbonate should give no test for *chloride* nor *sulphate* in very dilute nitric acid solution, with silver nitrate or barium nitrate. Tests with potassium sulphocyanate, or ammonium molybdate and nitric acid, should not show the presence of iron or phosphorus. Fusion with potassium cyanide in a current of carbon dioxide should give no dark sublimate of arsenic even on prolonged heating.

100 parts of water at

0°	C.	dissolve	7.1	parts	anhydrous	Na_2CO_3.*
10°	"	"	12.60	"	"	"
20°	"	"	21.4	"	"	"
30°	"	"	38.1	"	"	"
32.5°	"	"	59.	"	"	"
33°	"	"	46.2	"	"	"
79°	"	"	46.2	"	"	"
80°	"	"	46.1	"	"	"
90°	"	"	45.7	"	"	"
100°	"	"	45.4	"	"	"
105°	"	"	45.1	"	"	"

A maximum solubility is reached at 33° C. (46.2 parts) and remains nearly constant until about 79° C., above which there is a slight decrease.

* MULDER, Scheik. Verhand. **1864**, 129.

Specific gravity of $Na_2CO_3 + Aq$ at 17.5° C.*

Sp. gr.	% Na_2CO_3.	% $Na_2CO_3 \cdot 10\ H_2O$.
1.010	1	2.70
1.020	2	5.40
1.031	3	8.10
1.041	4	10.18
1.052	5	13.50
1.063	6	16.20
1.073	7	18.90
1.084	8	21.60
1.095	9	24.30
1.105	10	27.00
1.116	11	29.70
1.127	12	32.40
1.137	13	35.10
1.148	14	37.80
1.157	15	40.50

Specific gravity of $Na_2CO_3 + Aq$ at 30° C.†

Sp. gr.	Deg. Tw.	% Na_2CO_3.	Gr. Na_2CO_3 per liter of the solution.
1.140	28	13.62	155.3
1.150	30	14.47	164.4
1.160	32	15.32	177.7
1.170	34	16.18	189.3
1.180	36	17.04	201.1
1.190	38	17.90	214.0
1.200	40	18.76	225.1
1.210	42	19.61	237.3
1.220	44	20.47	249.7
1.230	46	21.33	262.3
1.240	48	22.21	275.4
1.250	50	23.08	288.5
1.260	52	23.93	301.5
1.270	54	24.78	314.7
1.280	56	25.62	327.9
1.290	58	26.46	341.3
1.300	60	27.30	354.9
1.310	62	28.13	368.5

* Hager, Commentar zum Pharmc. Germanica, **1883**.
† Lunge, Chemische Industrie, **1882**, 320.

84. SODIUM CHLORIDE.

$NaCl$. M.W. = 58.5.

Take of

Sodium chloride,	1000 gr.	
Water,	3500 cc.	
Lime (CaO),	12 gr.	
Barium chloride,	12–25 "	as needed.
Sodium carbonate, Hydrochloric acid,	each a sufficient quantity.	

Dissolve the salt in 3½ liters of cold water in a 14-inch evaporating dish. Add about 10 cc. more water to the lime than it will absorb, and let it stand until the slaking is complete. Mix the calcium hydrate with 100 cc. of water, to form a thin paste ("milk of lime"), add this to the salt solution, and warm. Filter, and pour dilute barium chloride solution into the hot filtrate, as long as a test shows any sulphuric acid not precipitated. Then, without filtering, carefully add a solution of sodium carbonate to precipitate the excess of barium and calcium salts. This usually requires about 10–12 gr. of dry sodium carbonate. Filter, and neutralize the excess of carbonate with hydrochloric acid, until neutral to litmus paper. Evaporate to crystallize. Dry the crystals in the dish on the steam bath and then in the hot closet.

Reactions:

$$MgCl_2 + Ca(OH)_2 = Mg(OH)_2 + CaCl_2.$$
$$MgSO_4 + BaCl_2 = BaSO_4 + MgCl_2.$$
$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2\ NaCl.$$
$$Na_2CO_3 + 2\ HCl = 2\ NaCl + CO_2 + H_2O.$$

Properties:

Sodium chloride is soluble in about 2.8 parts of water at 15° C., and this solubility does not change much with changes of temperature, as is shown in the following table:

100 parts of water at

0°	C.	dissolve	35.7	parts	sodium	chloride.*
10°	"	"	35.8	"	"	"
20°	"	"	36.0	"	"	"
30°	"	"	36.3	"	"	"
40°	"	"	36.6	"	"	"
50°	"	"	37.0	"	"	"
60°	"	"	37.3	"	"	"
70°	"	"	37.8	"	"	"
80°	"	"	38.4	"	"	"
90°	"	"	39.1	"	"	"
100°	"	"	39.8	"	"	"
109.7°	"	"	40.4	"	"	"

The specific gravity of salt solutions at 15° C. is shown in the following table:

1%	NaCl,	1.00725	sp. gr.†
10%	"	1.07335	"
20%	"	1.15107	"
25%	"	1.19228	"
26.395%	"	1.20433	"

Saturated solutions are precipitated by the addition of concentrated hydrochloric acid. The solution of pure salt in water, should be perfectly clear, and give no tests for *sulphates*, *alkaline earths*, nor *heavy metals*.

* MULDER, Scheik. Verhand. **1864**, 37.
† GERLACH, Zeit. anal. Chem. **8**, 279.

85. SODIUM NITRATE (C. P.).

$NaNO_3$. M.W. = 85.

Take of

Chilinitre,	1000 gr.
Water,	600 cc.

The crude nitre contains chlorides, bromides, iodides, and sulphates of sodium and magnesium, with traces of iron and alumina salts, and insoluble matter.

Dissolve the nitre in the water by heating to 85° C., add 50 cc. of "milk of lime,"* and digest for half an hour with frequent stirring. Filter, and acidify the hot filtrate with concentrated nitric acid; then add a solution of barium nitrate, in small portions, as long as test portions, filtered off and diluted, give a white precipitate with a drop of the barium nitrate. Filter hot, and neutralize the solution with sodium carbonate to precipitate any excess of calcium and barium salts added. Filter, and acidify the filtrate with concentrated nitric acid, 80° Tw. (sp. gr. 1.400), and heat to drive off carbon dioxide which may remain dissolved in the solution.

Then add about 100 cc. of concentrated nitric acid (80° Tw.), and cool rapidly, while stirring actively. Filter off the crystalline meal on the Büchner funnel (p. 14) with suction, and wash several times with dilute nitric acid, until free from chloride, etc. Redissolve the crystal meal in distilled water, evaporate to a density of 75° Tw. (sp. gr. 1.375), and allow to crystallize by cooling slowly. Filter out the crystals, and evaporate the mother liquor to saturation for another crop. Dry the

* Barium hydrate may be used instead of "milk of lime," but in this case there will be no necessity of adding barium nitrate. The excess of barium is then precipitated with sodium carbonate as above.

product in the warm closet, placing it in the cooler compartment at first.

Properties:

Sodium nitrate is somewhat deliquescent in damp air. 100 parts of water at

0° C.	dissolve	72.9	parts	nitrate.*
10° "	"	80.8	"	"
20° "	"	87.5	"	"
40° "	"	102.	"	"
60° "	"	122.	"	"
80° "	"	148.	"	"
100° "	"	180.	"	"
110° "	"	200.	"	"

The density of a solution of sodium nitrate at 20.2° C. containing

10%	$NaNO_3$	is	1.0676.†
20%	"	"	1.1418.
25%	"	"	1.1822.
30%	"	"	1.2239.
40%	"	"	1.3155.
50%	"	"	1.4180.

When heated above its melting point, sodium nitrate decomposes and passes into nitrite, and finally gives off nitrogen, oxygen, and nitrous vapors, leaving only caustic soda as residue. It is largely used to make potassium nitrate by double decomposition with potassium chloride or sulphate.

* MULDER, Scheik. Verhand. **1864**, 83

† SCHIFF, Ann. **110**, 75.

86. SODIUM NITROPRUSSIDE.*

$Na_2Fe(CN)_5NO \cdot 2\,H_2O$. M.W. = 298.

Take of

Potassium ferrocyanide,	200 gr.
Nitric acid, 83.5° Tw. (sp. gr. 1.42),	400 "
Sodium carbonate (anhydrous),	182 " (approx.)
Water,	285 cc.

Pulverize the ferrocyanide to a rather fine powder. Dilute the nitric acid with the water, in a 1000-cc. flat-bottom flask. Add the ferrocyanide to the diluted acid in small portions at a time, shaking the flask after each addition, and allowing the effervescence to cease before adding more ferrocyanide. *Do this under the hood!*

When all the ferrocyanide has been introduced, heat the flask on the water bath for an hour, until a test of 2 cc. of the solution gives no precipitate with ferric chloride. Then allow the flask to stand quietly in a cool place over night. Next day decant the olive green liquid from the crystals of potassium nitrate, pouring it through a Büchner funnel without filter paper, to remove any loose crystals. Neutralize the filtrate with the dry sodium carbonate introduced in small portions, shaking well after each addition.

When nearly neutralized cold, heat over the lamp to boiling, to expel carbon dioxide, and then complete the neutralization by adding a strong solution of sodium carbonate, a few cc. at a time, until there is no more effervescence. Avoid adding much excess of sodium carbonate. Filter hot, on a folded filter, to remove any blue or brown precipitate that may have formed during the neutralization. Evaporate the dark red filtrate in a

* Zeit. anorg. Chem. **11**, 278–287; Ber. **15**, 2613.

large casserole, on the water bath, until a considerable mass of crystals of nitroprusside has deposited from the hot liquid. Decant the *hot* mother liquor into a small casserole, leaving the mass of crystals, and dry them in a desiccator over sulphuric acid. Evaporate the mother liquor until more crystals separate from the hot liquid, and decant again. The crystals so obtained if not contaminated with nitrate, are dried as in the first case and put with the others. Evaporate the mother liquor from this second crystallization, to a very small bulk, and allow it to cool very slowly. A mixture of crystals of sodium and potassium nitrate, sodium nitroprusside, and any excess of sodium carbonate, is obtained, from which the red nitroprusside crystals may be picked out with pincers.

Redissolve the combined product of nitroprusside crystals, in about twice its weight of hot water, filter the solution through a folded filter into a 6-inch evaporating dish, and allow it to stand quietly for some time in a desiccator over sulphuric acid. By this very slow evaporation, large crystals of the nitroprusside may be obtained entirely free from the salts in the mother liquor. The progress of the crystallization should be watched from day to day, and the sulphuric acid renewed with concentrated acid every two or three days.

During the entire process of preparation and crystallization, the solution should be protected from direct sunlight and even from strong daylight.

Some authorities recommend the addition of three or four parts of alcohol to the solution of nitroprusside, just before allowing to crystallize, but in the author's experience this addition yielded no particular advantage.

Properties:

Sodium nitroprusside crystallizes in blood-red, rhombic prisms. It dissolves in $2\frac{1}{2}$ parts of cold water. The solution

is unstable, and on exposure to sunlight, decomposes, forming Prussian blue and liberating nitrogen oxides. A solution of sodium nitroprusside is used occasionally in the laboratory, as a delicate test for sulphides of the alkalies, in dilute solution with which it gives a deep violet coloration.

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87. SODIUM PHOSPHATE.

$Na_2HPO_4 \cdot 12\ H_2O$. M.W. = 358.

Take of

Bone ash (powdered),	5000 gr.
Sulphuric acid, 104° Tw. (sp. gr. 1.52),	3520 cc.
Sodium carbonate (dry),	2750 gr. (approx.)

The material used is bone ash which is very finely ground in a mill. Bone ash, when of good quality, may be reckoned as about 80% tricalcium phosphate, and requires for its decomposition

1.067 kg. H_2SO_4 of 104° Tw. (sp. gr. 1.520)
or 857 gr. H_2SO_4 of 140° Tw. (sp. gr. 1.700)
or 736 gr. H_2SO_4 of 160° Tw. (sp. gr. 1.800)

for each kilo of bone ash used.

Use a lead-lined tank, and place it out of doors in a good draught of air. Mix the acid (sp. gr. 104° Tw.) and 5 kg. of bone ash by means of a large porcelain spatula. Great heat is developed during the reaction, and water and acid fumes escape copiously. Stir well for an hour or two, and then let it stand over night to complete the decomposition of the ash. Lixiviate the mass with twice its volume of water, and boil by blowing in free steam. Filter hot, on a cloth bag filter (see FILTRATION, p. 10), and allow to drain. Repeat the boiling with fresh

water 5 or 6 times, until the wash water has a gravity of less than 2° Tw. Evaporate the filtrate to a convenient bulk, perhaps 6 liters, and neutralize the boiling-hot liquid with a strong solution of sodium carbonate of known strength. A heavy precipitate of calcium carbonate falls, which is filtered off, and the filtrate evaporated till the hot solution has a density of 25° Tw. at 17° C. Then let it stand quietly to crystallize. Drain the crystals, and recrystallize once or twice from distilled water. The crystals must be air dried after draining, and bottled as soon as possible, since they effloresce very quickly in the drying closet.

Reactions :

$$Ca_3P_2O_8 + 3\ H_2SO_4 + 6\ H_2O = 3\ (CaSO_4 + 2\ H_2O) + 2\ H_3PO_4.$$

$$Ca_3P_2O_8 + 2\ H_2SO_4 + 6\ H_2O = 2\ (CaSO_4 + 2\ H_2O) + (CaH_4P_2O_8 + H_2O).$$

$$H_3PO_4 + Na_2CO_3 = Na_2HPO_4 + H_2O + CO_2.$$

$$CaH_4P_2O_8 + 2\ Na_2CO_3 = 2\ Na_2HPO_4 + CaCO_3 + H_2O + CO_2.$$

Properties :

Sodium phosphate is soluble in water in the following proportions : 100 parts of water at

10°	C.	dissolve	3.9	parts	of	Na_2HPO_4.*
20°	"	"	9.3	"	"	"
25°	"	"	15.4	"	"	"
40°	"	"	63.9	"	"	"
50°	"	"	82.5	"	"	"
60°	"	"	91.6	"	"	"
75°	"	"	95.8	"	"	"
80°	"	"	96.6	"	"	"
99°	"	"	98.8	"	"	"
105°	"	"	82.5	"	"	"

* MULDER, Scheik. Verhand. **1864**, 103.

The crystals effloresce quickly in the air, and when heated to 100° C. all of the crystal water is given off.

As above prepared from common acid the salt may contain arsenic, copper or calcium sulphates, carbonates, chlorides, or nitrates.

The salt is used in the laboratory for the determination of magnesium and for the detection of the alkaline earth metals in general.

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88. SODIUM SULPHATE.

(Glauber's Salt.)

Na_2SO_4. M.W. = 142.

$Na_2SO_4 \cdot 10\ H_2O$. M.W. = 322.

To purify from iron:

Take of

Common Glauber's salts,	2000 gr.
Water,	3000 cc.
Milk of lime, Bleaching powder,	of each a small quantity.

(*a*) Dissolve the crude sodium sulphate in the water, and heat to boiling; add "milk of lime" until just alkaline. Stir well, and add, while stirring actively, a solution of bleaching powder, in *small portions* at a time, until a test of 10 cc. filtered off shows no traces of iron. The solution must be kept very hot until all the iron is precipitated, so that the precipitate may be dense and settle rapidly. Decant (p. 19) the clear liquor through a cloth filter, and evaporate the filtrate to a density of 51.5° Tw. (sp. gr. 1.257) taken at 40° C. Allow it to stand quietly until cold, and large crystals of Glauber's salt deposit. Free these from the mother liquor in the centrifugal machine. Evaporate the mother liquor for another crop of crystals; these

may be contaminated with chlorides and should be recrystallized from distilled water.

(*b*) The oxidation of the iron may be accomplished by putting chlorine water into the hot, concentrated solution of Glauber's salt; then add caustic soda solution, a little at a time, till all the iron is precipitated. Filter, and evaporate to crystallize as above described.

Properties:

The crystals of Glauber's salts effloresce when exposed to dry air and melt in their "water of crystallization," when heated to 33° C. A solution of this salt reaches its maximum concentration at 34° C., beyond which point the solubility decreases and the anhydrous salt separates.

100 parts of water dissolve at

Temp.	Na_2SO_4.*	$Na_2SO_4 \cdot 10\ H_2O$.†
0. ° C.	4.8	12.16
10. ° "	9.0	23.04
15. ° "	13.4	35.96
20. ° "	19.5	58.85
25. ° "	27.9	98.48
30. ° "	40.9	184.1
32. ° "	47.8	—
33. ° "	50.6	323.1
34. ° "	50.4	412.2
35. ° "	50.2	
40. ° "	48.8	Salt melts in its water of crystallization above 34° C.
45. ° "	47.7	
50. ° "	46.7	
55. ° "	45.9	
60. ° "	45.3	
65. ° "	44.8	
70. ° "	44.4	
75. ° "	44.0	
80. ° "	43.7	
85. ° "	43.3	
90. ° "	43.1	
95. ° "	42.8	
100. ° "	42.5	
103.5° "	42.2	

* MULDER, Scheik. Verhand. **1864**, 123.
† LÖWEL, Ann. Chim. Phys. [3] **49**, 42.

Specific gravity of $Na_2SO_4 + Aq$ at 15° C.*

%	$Na_2SO_4 + 10\ H_2O$.	Na_2SO_4.	
1	1.004	1.0091	
2	1.008	1.0182	
3	1.013	1.0274	
4	1.016	1.0365	
5	1.020	1.0457	
6	1.024	1.0550	
7	1.028	1.0644	
8	1.032	1.0737	
9	1.036	1.0832	
10	1.040	1.0927	
15	1.060		
20	1.082		
25	1.103		
30	1.125		

89. SODIUM SULPHIDE.

$Na_2S \cdot 9\ H_2O$. M.W. = 240.

Take of

Caustic soda,	200 gr.
Water,	200 cc.

Dissolve the caustic in the water in a loosely stoppered flask or bottle. Allow it to stand quietly until the sediment collects on the bottom of the vessel, and then decant through a filter of glass wool. The clear solution should have a density of 80° Tw. (sp. gr. 1.400) at 20° C.

Divide the solution into 2 *equal* portions, and transfer one portion to a 300-cc. flask. Into this portion pass a moderately rapid stream of hydrogen sulphide, which has passed through a wash bottle containing water. The color of the caustic solution changes to deep yellow, a white precipitate settling out at

* GERLACH, Zeit. anal. Chem. 8, 287.

first; but on continuing the stream of hydrogen sulphide, the solution becomes warm, the precipitate redissolves, and the color of the solution becomes red or brown. During this saturation of the liquid, a considerable increase in the volume of the solution will be noticed. When the saturation is complete, the temperature falls, and the odor of hydrogen sulphide persists after shaking the flask, blowing out the air in it, and allowing it to stand.

Mix the remaining half of the caustic solution in an 8-inch evaporating dish, with the solution of sodium sulphydrate obtained as above described, and heat on the water bath for half an hour, stirring frequently. A white crystalline precipitate of needle-like crystals separates when the solutions are mixed, but dissolves on heating. Put the dish under a bell jar, and allow it to stand over night at the temperature of the room. Pour off the supernatant mother liquor from the solid cake of sodium sulphide, and allow it to drain well. Break up the crystalline mass, and dry it in a desiccator over sulphuric acid, until the thin edges of the crystals begin to effloresce. Put into a dry, well-stoppered bottle, and keep in a cool place.

The crystals thus prepared are colorless or slightly red or brown. If desired, they may be redissolved in a little warm distilled water, about 20% alcohol added to the solution, and then allowed to recrystallize.

Reactions:

$$NaOH + H_2S = NaSH + H_2O.$$
$$NaSH + NaOH = Na_2S + H_2O.$$

Properties:

Sodium monosulphide crystallizes from the above solution in large, quadratic crystals with 9 H_2O. The substance is very soluble in water, has a strong alkaline reaction, and yields a colorless solution which, when acidified with hydrochloric acid,

sets free hydrogen sulphide, with only a slight milkiness in the liquid. A yellow or orange precipitate, after acidifying, indicates the presence of arsenic or antimony. If the solution of the sodium sulphide in water is yellow, there are polysulphides of sodium present.

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90. SODIUM SULPHITE.*

$Na_2SO_3 + 7\ H_2O$. M.W. = 252.

Make a concentrated solution of sodium carbonate, and divide it into 2 equal parts. Saturate one portion with sulphur dioxide gas while hot, add the other portion (also hot), and let the mixed solutions cool. The salt crystallizes in large, colorless crystals, which must be drained or "centriffed," and bottled quickly.

Reactions:

$$Na_2CO_3 + 2\ SO_2 + H_2O = 2\ NaHSO_3 + CO_2.$$
$$2\ NaHSO_3 + Na_2CO_3 = 2\ Na_2SO_3 + 2\ H_2O + CO_2.$$

Properties:

Sodium sulphite is very soluble in water, the point of greatest solubility being 33° C. The solution is strongly alkaline. The crystals effloresce quickly on exposure to the air, and more or less oxidation occurs. When heated to 150° C., the "water of crystallization" is driven off, but the salt does not melt until the temperature rises considerably above 150° C.

The salt is much used as a preservative, and as a reducing substance in photography; also as an "anti-chlor" to remove traces of chlorine from bleached fibers.

* RÖHRIG, J. pr. Chem. **145** (1888), 222. RAMMELSBERG, Ann. **50**, 259; **64**, 240.

91. SODIUM THIOSULPHATE (Hyposulphite).

$Na_2S_2O_3 \cdot 5\,H_2O$. M.W. = 248.

This salt is formed by boiling "flowers of sulphur" in a solution of sodium sulphite (p. 207) for a considerable time. When no more sulphur dissolves, filter, evaporate the filtrate to 51° Tw. (sp. gr. 1.256), and let it crystallize.

Reaction:

$$Na_2SO_3 + S = Na_2S_2O_3.$$

Properties:

Sodium thiosulphate forms large, colorless crystals which effloresce when exposed to the air; when heated to 48° C., the crystals melt in their "water of crystallization," and when heated to 215° C., the water is all driven off; at 220° C. the salt decomposes and the sulphur separates.

100 parts of water at

0° C.	dissolve	47.60	parts	of the	anhydrous	salt.*
20° "	"	69.50	"	"	"	"
40° "	"	104.2	"	"	"	"
60° "	"	192.30	"	"	"	"

100 parts of water at 19.5° dissolve 171 parts of the crystallized salt. On standing, the aqueous solution slowly decomposes, with separation of sulphur and formation of sulphite, which, in turn, is slowly oxidized to sulphate on exposure to the air.

The specific gravity of solutions of sodium thiosulphate is shown in the following table:

* KREMERS, Pogg. Ann. **99**, 50.

Sp. gr.	% $Na_2S_2O_3 \cdot 5\,H_2O$.	% $Na_2S_2O_3$.
1.0052*	1	0.637
1.0264	5	3.185
1.0529	10	6.371
1.0807	15	9.556
1.1087	20	12.742
1.1381	25	15.927
1.1676	30	19.113
1.1986	35	22.298
1.2297	40	25.484
1.2624	45	28.669
1.2954	50	31.855

Sodium thiosulphate solution dissolves the iodides and bromides of silver, mercury, and lead, forming soluble double salts.

It is largely used as an "anti-chlor" for bleached fibers and as a solvent for the silver bromide and chloride in photography.

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92. STANNIC CHLORIDE.

$SnCl_4$. M.W. = 260.

(*a*) Take of

Stannous chloride (crystals),	1000 gr.
Hydrochloric acid, 25° Tw. (sp. gr. 1.125),	1170 cc.
Nitric acid, 44° Tw. (sp. gr. 1.220),	435 "
Water,	1000 "

Put the stannous chloride into a 12-inch evaporating dish, and add the 1170 cc. of hydrochloric acid; warm on the steam bath, and stir until the salt is dissolved. Then dilute with 1 liter of hot water. If the solution does not remain clear, there is a deficiency of hydrochloric acid, in which case add very concentrated hydrochloric acid, a few drops at a time,

* H. Schiff, Ann. **113**, 188.

until the solution becomes clear. Add the nitric acid, a few cc. at a time, to the warm solution, stirring well after each addition. After a considerable part of the nitric acid has been added, test a few drops of the solution with a drop of mercuric chloride solution. If a white precipitate falls, stannous chloride is present, and more nitric acid is needed. $SnCl_2 + 2\ HgCl_2 = SnCl_4 + 2\ HgCl$. When no white precipitate falls, the oxidation is complete, and no more nitric acid should be added. Put the liquid product into a tightly stoppered bottle.

Reaction:

$$3\ SnCl_2 \cdot 2\ H_2O + 6\ HCl + 2\ HNO_3 = 3\ SnCl_4 + 10\ H_2O + 2\ NO.$$

Instead of using nitric acid, the stannous chloride may be treated with chlorine gas or with hydrochloric acid and potassium chlorate, in the proportions required in the following reactions:

$$SnCl_2 \cdot 2\ H_2O + Cl_2 = SnCl_4 + 2\ H_2O.$$
$$3\ SnCl_2 \cdot 2\ H_2O + 6\ HCl + KClO_3 = 3\ SnCl_4 + KCl + 9\ H_2O.$$

(*b*) For anhydrous stannic chloride:*

Heat 150 gr. of granulated or bar tin, in a tubulated retort, on the gas stove until melted, and lead a strong stream of dry chlorine gas into the retort through a glass tube which opens just above the surface of the melted tin. To the neck of the retort join a long condenser, which connects with two Wolff's bottles acting as receivers, and placed in a pan of ice-water to condense the volatile stannic chloride. Then distill the stannic chloride collected in the Wolff bottles, from a fractionation flask provided with a thermometer and containing some bits of tin foil. The distillate coming over between

* Bender and Erdmann, Chemische Präparatenkunde, 1, 435.

112–114° C. is pure; this should be collected in the glass-stoppered bottle in which it is to be preserved.

Reaction:

$$Sn + 2\,Cl_2 = SnCl_4.$$

Properties:

Stannic chloride is a colorless or faintly yellow liquid, which fumes on exposure to the air and boils at 114° C. When mixed with small quantities of water, crystallized salts, such as $SnCl_4 \cdot 3\,H_2O$ and $SnCl_4 \cdot 5\,H_2O$, are formed. These are very soluble in water. The dilute aqueous solution, when boiled, yields a precipitate of stannic acid, H_2SnO_3.

The specific gravity of the aqueous solution at 15° C. containing

2%	$SnCl_4 \cdot 5\,H_2O$	is	1.012.*
10%	"	"	1.059.
20%	"	"	1.124.
30%	"	"	1.195.
40%	"	"	1.276.
50%	"	"	1.366.
60%	"	"	1.468.
70%	"	"	1.587.
80%	"	"	1.727.
90%	"	"	1.894.
95%	"	"	1.988.

Stannic chloride solutions prepared as in (*a*) are largely used in the dyeing and printing of cotton and silk. It forms double salts with the alkali chlorides, which are easily crystallized; the most important of these is the stannic-ammonium chloride, formerly much used as a mordant under the name of "pink salt." Mixtures of stannic and stannous chlorides are found in commerce under such names as "tin spirits," "cotton spirits," "oxymuriate of tin," "pink-cutting liquor," etc.

* GERLACH, Dingl. J. **178**, 49.

93. STANNOUS CHLORIDE.

$SnCl_2 \cdot 2\,H_2O$. M.W. = 225.

Take of

Tin,	500 gr.
Hydrochloric acid, 36° Tw. (sp. gr. 1.180),	750 cc.

"Feather" the tin, as directed on page 86, and put into a deep beaker of at least 1200-cc. capacity, and add the hydrochloric acid in portions of about 75 cc. each. Heat gently until the reaction starts, and allow to stand, covered with a watch glass, on the steam table until the reaction moderates before adding the next portion. When about one-half of the acid has been added, let the beaker stand quietly, keeping it hot until all action ceases. Decant the solution of stannous chloride from the residue of tin, and add the remainder of acid as above directed. Heat on the steam bath until the tin is all dissolved, or the acid all neutralized. Allow to settle, and decant the liquid from any residue. Combine the two solutions, evaporate to a specific gravity of 1.985, and let the liquid cool in a covered evaporating dish. Drain the mass of crystals in a funnel covered with a watch glass. Dry in a desiccator over sulphuric acid, and bottle as soon as dry.

Care must be taken to protect the preparation from dust during the entire process, and to keep the vessels covered to exclude the air as much as possible. If filtration is necessary, use glass wool. No water should be added to the solution at any time, for turbidity may result, due to the formation of oxychloride of tin.

Reaction:

$$Sn + 2\,HCl = SnCl_2 + H_2.$$

Properties:

Stannous chloride forms colorless crystals with $2\,H_2O$, which are sold in commerce under the name of "tin crystals."

It is very soluble in water, dissolving in 0.37 parts of water at 15° C.

The specific gravity of the aqueous solution at 15° C. containing

5%	$SnCl_2 \cdot 2\ H_2O$	is	1.0331.*
10%	"	"	1.0684.
20%	"	"	1.1442.
25%	"	"	1.1855.
30%	"	"	1.2300.
35%	"	"	1.2779.
40%	"	"	1.3298.
50%	"	"	1.4451.
60%	"	"	1.5823.
70%	"	"	1.7452.
75%	"	"	1.8399.

The aqueous solution absorbs oxygen from the air and becomes turbid, owing to the formation of oxychloride, $3\ SnCl_2 + H_2O + O = SnCl_4 + 2\ SnCl(OH)$. The crystals also decompose in this way when exposed to the air. The oxychloride is dissolved by the addition of hydrochloric acid.

The salt is largely used in dyeing textile fabrics and somewhat as a reducing agent in analytical work. Commercial samples often contain arsenic, alkaline earths (magnesium, etc.), and sulphates.

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94. STRONTIUM CHLORIDE.

$SrCl_2 + 6\ H_2O$. M.W. = 266.

(*a*) Take of

Strontianite (powdered),	1000 gr.
Hydrochloric acid, 37° Tw. (sp. gr. 1.185),	1150 cc.
Strontium hydrate,	25 gr.
Water,	500 cc.

* GERLACH, Dingl. J. **186**, 131.

Put the strontianite into a 14-inch evaporating dish, add water, and stir to form a thick cream. Put the dish on the steam bath, and heat; then add the acid in the same way as directed in the preparation of barium chloride on page 76, keeping the solution hot. When all the acid has been added, bring to boiling to drive off carbon dioxide, and then add 25 gr. strontium hydrate to the hot solution and keep hot for an hour, stirring frequently. Filter to remove the insoluble residue and precipitated iron and alumina, and acidify the filtrate with hydrochloric acid; concentrate to a density of 60° Tw. (sp. gr. 1.300), and allow to cool and crystallize where it will not be disturbed. Drain or pass the crystals through the centrifugal machine. Dry in the desiccator. The mother liquor will yield more crystals on further concentration.

Reaction:

$$SrCO_3 + 2\ HCl = SrCl_2 + H_2O + CO_2.$$

(*b*) Take of

Celestite (powdered),	300 gr.
Charcoal "	100 "

Mix the finely powdered materials very thoroughly, and fill a Battersea G crucible with the mixture, pressing it down firmly and covering it with a layer of powdered charcoal. Then fit a sheet-iron cover *tightly* over the crucible by pressing down the cut edges over its sides. Then heat in the Roessler furnace for an hour or more at a full white heat. Cool the crucible before opening it. When cold, transfer the contents to an evaporating dish, and add dilute hydrochloric acid until the evolution of hydrogen sulphide becomes slow. Heat to

boiling until all the hydrogen sulphide is expelled. Filter the solution, and evaporate to crystallize as in (*a*).

Reactions:

$$SrSO_4 + 4\ C = SrS + 4\ CO.$$
$$SrS + 2\ HCl = SrCl_2 + H_2S.$$

(*c*) Strontianite usually contains barium and calcium carbonates, and the above methods do not separate these completely. A pure salt may be prepared as follows: *

Treat strontianite, or sulphide obtained by the reduction of the sulphate, with just enough hydrochloric acid to dissolve it, preferably using a slight excess of the salt so that all the acid may be neutralized. Add a slight excess of ammonia to precipitate iron and alumina, filter, and add excess of sulphuric acid. Wash the precipitate of barium, calcium, and strontium sulphates by decantation, with very dilute sulphuric acid (1–2% H_2SO_4), and then wash with water until the calcium and magnesium salts are removed. Digest cold for two days with a 10% solution of ammonium or potassium carbonate, stirring frequently and thoroughly. Wash by decantation (p. 20) with water a number of times. Digest the mixture of carbonate and sulphate thus obtained, with dilute hydrochloric acid, which dissolves the strontium carbonate and a trace of barium salt. Decant, allow the solution to stand 24 hours or more, and filter through a filter moistened with hydrochloric acid. To each liter of the filtrate add 200 gr. of hydrochloric acid (sp. gr. 1.17) and 2–3 gr. of precipitated strontium sulphate, which need not be free from barium, and let the whole stand for several hours, stirring at frequent intervals. This precipitates the barium completely, a corresponding amount of strontium going into solution. Filter, evaporate to dryness, extract the residue with 3 times its weight of water, allow it to stand a

* BARTHE and FALIERES, Bull. Soc. Chim. [3] **7** **(1892)**, 104.

day, and filter again. Evaporate the solution until the strontium chloride crystallizes out.*

Properties:

Strontium chloride forms long deliquescent crystals with 6 H_2O, which pass off when the salt is heated to 100° C.

100 parts of water at

0° C.	dissolve	44.2	parts	$SrCl_2$.†
10° "	"	48.3	"	"
20° "	"	53.9	"	"
30° "	"	60.	"	"
40° "	"	66.7	"	"
50° "	"	74.4	"	"
60° "	"	83.1	"	"
70° "	"	89.6	"	"
80° "	"	92.4	"	"
90° "	"	96.2	"	"
100° "	"	101.9	"	"
110° "	"	109.1	"	"
118° "	"	115.5	"	"

The specific gravity of the aqueous solution at 15° C. containing

5%	$SrCl_2$	is	1.0453.‡
10%	"	"	1.0929.
15%	"	"	1.1439.
20%	"	"	1.1989.
25%	"	"	1.2580.
30%	"	"	1.3220.
33%	"	"	1.3633.

Strontium chloride is also soluble in alcohol.

* According to Sörensen (Zeit. anal. Chem. **11**, 305), the above process does not yield a product entirely free from barium. The method which he gives, however, is very complicated, and beyond the scope of this Manual. The original memoir should be consulted by the student.

† Mulder, Scheik. Verhand. **1864**, 118.

‡ Gerlach, Zeit. anal. Chem. **8**, 283.

95. STRONTIUM NITRATE.

$Sr(NO_3)_2$. M.W. = 211.
$Sr(NO_3)_2 \cdot 4\ H_2O$. M.W. = 283.

Take of

Strontianite (powdered),	1000 gr.
Nitric acid, 50° Tw. (sp. gr. 1.250),	1700 cc.
Strontium hydrate,	25 gr.
Water,	1500 cc.

Put the finely powdered strontianite into a 14-inch evaporating dish, and add water to make a thick cream. Warm on the steam bath, and add the nitric acid in small portions and with the same precautions as in the preparation of barium nitrate on page 80. When the acid has all been added, and the action has ceased in the warm solution, heat until all the carbon dioxide is expelled; then add 25 gr. of strontium hydrate, and warm for an hour or two, stirring well at frequent intervals. Filter off the undissolved residue and the precipitated iron and alumina, make the solution just acid with nitric acid, concentrate to a density of 75° Tw. (sp. gr. 1.375), and set away to crystallize. Concentrate the mother liquor further for more crystals. Drain the crystals, or, better, run them through the centrifugal machine, and dry very slightly in the desiccator until they begin to effloresce, when they should be bottled at once.

Or, preferably, the solution of nitrate obtained above, may be evaporated directly down nearly to dryness, and the small quantity of mother liquor poured off while hot. By this method, anhydrous crystals are formed from the hot concentrated solution.

Reaction:

$$SrCO_3 + 2\ HNO_3 = Sr(NO_3)_2 + H_2O + CO_2.$$

Properties:

Strontium nitrate forms transparent, anhydrous crystals from hot concentrated solution, but by cooling a moderately dilute solution, the crystals contain 4 H_2O and effloresce very quickly.

The anhydrous salt is very soluble in water. 100 parts of water at

0° C.	dissolve	39.5	parts	$Sr(NO_3)_2$.*
10° "	"	54.9	"	"
20° "	"	70.8	"	"
30° "	"	87.6	"	"
40° "	"	91.3	"	"
50° "	"	92.6	"	"
60° "	"	94.0	"	"
70° "	"	95.6	"	"
80° "	"	97.2	"	"
90° "	"	99.0	"	"
100° "	"	101.1	"	"
107° "	"	102.7	"	"

The specific gravity of the aqueous solution at 19.5° C. containing

1%	$Sr(NO_3)_2$	is	1.009.†
5%	"	"	1.041.
10%	"	"	1.085.
15%	"	"	1.131.
20%	"	"	1.181.
25%	"	"	1.233.
30%	"	"	1.292.
35%	"	"	1.354.
40%	"	"	1.422.

Strontium nitrate finds some use in pyrotechnics because of the brilliant red color it imparts to flame. When heated to redness, the nitrate decomposes into the oxide.

* MULDER, Scheik. Verhand. **1864**, 114.

† GERLACH, Zeit. anal. Chem. **8**, 286.

96. STRONTIUM OXIDE.

SrO. M.W. = 103.

Strontium Hydrate.

$Sr(OH)_2$. M.W. = 121.

$Sr(OH)_2 \cdot 8\,H_2O$. M.W. = 265.

Strontium oxide is best prepared by igniting the dry strontium nitrate at a red heat for an hour or two, in the Roessler furnace.

To form the hydrate:

(*a*) Treat the oxide as above prepared with 1.6 parts of water, in consequence of which the whole mixture becomes a solid crystalline mass. By redissolving in 5 parts of boiling water, filtering, and allowing the filtrate to cool slowly, transparent crystals of the hydrate are obtained.

(*b*) * Or the strontium sulphide obtained by reducing strontium sulphate with charcoal or pitch in the same way as directed for barium sulphide in (*b*), page 77, may be converted to the hydrate by the following process:

Take the product obtained by the reduction of 150 gr. of celestite and stir it up in a 14-inch evaporating dish with 1 liter of boiling water. To the boiling mixture add copper scales (which have previously been moistened with nitric acid and then ignited), until a test portion filtered off gives no brownish black precipitate with lead acetate solution. Filter hot into a beaker. Boil the residue with 100 cc. of water, and filter this into the same beaker. Cover carefully, and allow to stand 24 hours to crystallize. Pour off the mother liquor, evaporate to a volume of 300 cc., and cool for more crystals. Run the crystals through the centrifugal machine, or dry them on porous plates of biscuit porcelain (p. 27). Bottle at once in a well-stoppered bottle.

* Bender and Erdmann, Präparatenkunde, I, 37.

Reaction :

$$SrS + CuO + H_2O = Sr(OH)_2 + CuS.$$

Properties :

Strontium oxide is a dirty white porous substance, which combines directly with water with the evolution of heat.

Strontium hydrate forms a gray crystalline mass or transparent crystals, according to the mode of preparation. When heated to 100°, the crystals give off their water of crystallization, leaving the hydrate $Sr(OH)_2$, which fuses at a low red heat unchanged, but at a higher temperature is converted into the oxide. The crystallized hydrate is deliquescent and soluble in water, forming a strongly alkaline solution. 1 part dissolves in 50 parts of water at 16° and in 2 parts of boiling water. The solution absorbs carbon dioxide from the air with avidity and soon becomes turbid, if exposed.

Strontium hydrate is extensively used in the beet-sugar industry for the recovery of sugar from the molasses.

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97. SULPHUR DIOXIDE.

SO_2. M.W. = 64.

Take of

Copper chips or turnings,	100 gr.
Sulphuric acid (concentrated),	300 "

Put the copper into a 1500-cc. round-bottom flask provided with a rubber stopper, carrying a thistle tube and a delivery pipe. Connect the delivery pipe with a 500-cc. bottle containing 200 cc. of water, and provided with a safety tube and a delivery pipe, through which the sulphur dioxide may be led

into water or other liquid, which is to be saturated. The acid must not entirely cover the copper.

Warm the flask until the reaction begins, and then remove the lamp, as the heat generated is sufficient to maintain the reaction. When the water in the wash bottle is saturated, a strong flow of gas will be supplied by the apparatus until the acid is exhausted, or the copper dissolved. A dish should be placed under the flask to catch its contents if it should break.

Reaction:

$$Cu + 2\ H_2SO_4 = CuSO_4 + 2\ H_2O + SO_2.$$

Properties:

Sulphur dioxide is a colorless gas, of suffocating odor, soluble in water, forming sulphurous acid. It is a powerful bleaching agent for wool, silk, or straw which has been moistened with water. It is often used as a reducing agent.

Sulphurous acid and certain acid sulphites, are used as preservative agents and disinfectants.

The solution of copper sulphate formed in the flask may be used in the preparation of that salt (p. 105).

The solubility of SO_2 in water at various temperatures and reduced to 760-mm. pressure is shown in this table: *

Temp.	Vols. of SO_2 reduced to 0° and 760 mm. contained in 1 vol. of sat. SO_2 + Aq.	Vols. of SO_2 reduced to 0° and 760 mm. dissolved by 1 vol. H_2O under 760-mm. pressure.
0	68.861	79.789
5	59.816	67.485
10	51.383	56.647
15	43.564	47.276
20	36.206	39.374
25	30.766	32.786
30	25.819	27.161
35	21.234	22.489
40	17.013	18.766

* SCHÖNFELD, Ann. **95**, 5.

98. ZINC CARBONATE.*

$ZnCO_3$. M.W. = 125.

Take of

Zinc sulphate (purified),	1000 gr.
Sodium bicarbonate (dry),	625 "
Water,	4200 cc.

Dissolve the sodium bicarbonate in 3500 cc. of hot water, in a 14-inch evaporating dish, and heat to boiling. Dissolve the zinc sulphate in 700 cc. of hot water, and filter, if necessary, directly into the boiling solution of sodium bicarbonate, regulating the flow of the filtrate so that the boiling of the bicarbonate solution is not interrupted. When all the zinc sulphate has been added, allow the precipitate of zinc carbonate to settle, and decant the liquor, which contains sodium sulphate. Wash the carbonate with boiling water by decantation, until free from sulphate, and then collect in a cloth filter, press out the excess water, and dry in the warm closet.

If the sodium bicarbonate be added to the zinc sulphate, a precipitate of basic carbonates of zinc is thrown down, which is very difficult to decompose by the further addition of sodium bicarbonate. An excess of sodium bicarbonate must be present in any case. If the precipitation is done cold, the precipitate is very voluminous and difficult to wash.

Reaction:

$$ZnSO_4 \cdot 7\ H_2O + 2\ NaHCO_3 = ZnCO_3 + Na_2SO_4 + 8\ H_2O + CO_2.$$

Properties:

Zinc carbonate is a pure white powder, insoluble in cold water, but dissolving easily in caustic alkalies, forming zincates, which are soluble.

* MOHR, Arch. Pharm. [2] 65, 136.

The precipitate, as obtained by the above process, contains a little basic carbonate. (Potassium bicarbonate is said to yield a pure zinc carbonate.) By using normal carbonate of sodium, the precipitate formed is a basic salt of varying composition.

By igniting zinc carbonate at a red heat, carbon dioxide and water are driven out and pure zinc oxide remains.

The salt should dissolve in hydrochloric acid, yielding a solution which is not changed by hydrogen sulphide (absence of *arsenic*, *cadmium*, *copper*, *lead*, etc.), and in which ammonium carbonate forms a white precipitate, completely soluble without residue, in an excess of the reagent (absence of *iron*, *aluminum*, *calcium*, etc.). No lead should be shown by the addition of sulphuric acid.

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99. ZINC CHLORIDE.

$ZnCl_2$. M.W. = 136.

Take of

Zinc (metallic),	1000 gr.
Hydrochloric acid, 36° Tw. (sp. gr. 1.180),	2600 cc.
Water,	1000 "

Mix the acid and water in a 14-inch evaporating dish, or in a 2-gallon crock, and add the zinc in scraps, as fast as it may be done without causing the contents of the dish to froth over, owing to the vigorous effervescence, due to the liberation of hydrogen. Toward the last, when the action becomes slow, heat the dish on the steam bath until the action ceases. A residue of some excess zinc and a black insoluble matter remains. The excess of zinc is necessary to prevent the solution of copper and arsenic. Let the solution stand until the sediment deposits, and decant the liquid through a filter

of asbestos or glass wool. Purify the clear liquid from iron as directed under zinc sulphate on page 225. Filter off the precipitated iron and zinc, and evaporate the filtrate over the lamp, until the temperature of the liquid mass rises to 240° C. If discolored by the presence of organic matter, a little potassium chlorate may be cautiously added to the hot liquor. By carefully adding a few drops of hydrochloric acid to the hot liquid while stirring actively, any basic salts may be dissolved. This operation needs *much care*, and the hands should be protected by gloves from spatters of the zinc chloride; otherwise serious burns may result.

Cast the fused zinc chloride into sticks, in a smooth iron mould, or it may be allowed to solidify in a porcelain dish and the resulting cake broken up into lumps of convenient size, and bottled at once while still quite warm. The bottle should be tightly stoppered and the cork covered with melted paraffine.

Reaction:

$$Zn + 2\ HCl = ZnCl_2 + H_2.$$

Properties:

Zinc chloride is a white, very deliquescent substance which has a strong affinity for water. It has a very corrosive action on organic matter and hence is used as a caustic in medicine. It unites with alkaline chlorides to form double salts, of which the zinc-ammonium salt is the most important. This $(NH_4)_2ZnCl_3$ is much used in solution as "soldering liquor," as it dissolves metallic oxides and cleans the surface of the metal.

Zinc chloride is very soluble in water, dissolving in about 0.3 parts at 19° C. From a very concentrated solution containing hydrochloric acid, crystals of $ZnCl_2 \cdot H_2O$ may be obtained. The aqueous solution, when boiled, gives off some hydrochloric acid, forming oxychloride of zinc, ZnCl(OH).

The salt is largely used in the arts as a water-absorbing substance, as a preservative agent for wood, and in the size for cotton goods. Its use in the laboratory is chiefly as a dehydrating substance.

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100. ZINC SULPHATE.

$ZnSO_4 \cdot 7\,H_2O$. M.W. = 287.

Take of

Zinc (metallic),	1000 gr.
Sulphuric acid, 166° Tw. (sp. gr. 1.83),	1625 cc.
Water,	4500 "

Mix the water and acid in a 16-inch evaporating dish, or in a 2-gallon crock. Add scraps of zinc slowly, taking care that the vigorous effervescence does not cause the contents of the dish to froth over the top. No heating is necessary, sufficient heat being set free by the combination between the zinc and the acid. When the action becomes more moderate, keep the dish at about 90° C. on the steam bath until all action ceases. The metal should be nearly all dissolved, leaving a small amount of insoluble black residue. A small excess of zinc is used to render the solution as neutral as possible and to prevent the solution of any arsenic, copper, or lead which may be present as impurities. Allow the solution to stand quietly until the sediment has deposited, and decant through a glass-wool or asbestos filter (p. 12).

The clear solution may contain iron, and if it is desired to have it entirely free from iron, a stream of chlorine gas (p. 39) may be passed into the solution until it smells strongly of the gas. Then add to the hot liquid, a strong solution of sodium

carbonate, a few drops at a time, while stirring actively, until the precipitate produced has a light brown color. Then digest for an hour or so at a moderate warmth. The iron and manganese are precipitated, together with some of the zinc, leaving the solution quite pure.

Filter, and evaporate the filtrate to a density of 90° Tw. (sp. gr. 1.450), and allow to crystallize slowly. Drain the crystals in a covered funnel, or run them through the centrifugal machine. Dry at a low temperature in the drying closet, turning the mass over several times while drying. Bottle at once when dry. The mother liquor should yield more crystals on further evaporation.

Reaction :

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

Convenient sources for zinc are the old "crow's feet" and coils of exhausted battery cells. The chief impurities are copper, lead, and iron.

Chemically pure zinc does not dissolve freely in sulphuric acid, but the addition of a few drops of chloroplatinic acid solution will start the reaction.

Properties :

Zinc sulphate forms transparent, needle-like crystals or prisms containing 7 H_2O. They effloresce quickly in dry air, and when heated to 100° C., lose 6 molecules of crystal water. The seventh molecule escapes at about 300° C. At a low red heat the anhydrous salt is decomposed, and zinc oxide is formed.

The salt is known in commerce as "white vitriol," and is extensively used in the arts for weighting cotton goods and in wool-dyeing. It is also used somewhat in medicine and as a preservative agent and antiseptic.

The crystallized salt is very soluble in water. 100 parts of water at

0° C.	dissolve	115.22	parts	$ZnSO_4 \cdot 7\ H_2O$.*
10° "	"	138.21	"	"
20° "	"	161.49	"	"
30° "	"	190.90	"	"
40° "	"	224.05	"	"
50° "	"	263.84	"	"
60° "	"	313.48	"	"
70° "	"	369.36	"	"
80° "	"	442.62	"	"
90° "	"	533.02	"	"
100° "	"	653.59	"	"

The specific gravity of the aqueous solution at 15° C. containing

1%	$ZnSO_4 \cdot 7\ H_2O$	is	1.006.†
5%	"	"	1.0288.
10%	"	"	1.0593.
20%	"	"	1.1236.
30%	"	"	1.1933.
40%	"	"	1.2709.
50%	"	"	1.3532.
60%	"	"	1.4451.

According to Mulder,‡ zinc sulphate solutions decompose when heated over 40° C., forming basic salts.

* Poggiale, Ann. Chim. Phys. [3] **8**, 467.
† Gerlach, Zeit. anal. Chem. **8**, 288.
‡ Scheik. Verhand. **1864**, 74.

APPENDIX.

Approximate Atomic Weights and Valence of the Elements.

Aluminum	Al III	27.5	Niobium (Colum-		
Antimony	Sb III V	122	bium)	Nb III V	94
Arsenic	As III V	75	Nitrogen	N III V	14
Barium	Ba II	137	Osmium	Os IV VI	199
Beryllium	Be II	9.4	Oxygen	O II	16
Bismuth	Bi III V	208	Palladium	Pd II IV VI	106
Boron	B III	11	Phosphorus	P III V	31
Bromine	Br I VII	80	Platinum	Pt II IV VI	197.18
Cadmium	Cd II	112	Potassium	K I	39
Caesium	Cs I	133	Rhodium	Rh II IV VI	104
Calcium	Ca II	40	Rubidium	Rb I	85
Carbon	C IV II	12	Ruthenium	Ru IV VIII	104
Cerium	Ce IV	137	Scandium	Sc IV	44
Chlorine	Cl I VII	35.5	Selenium	Se II IV VI	79
Chromium	Cr II III VI	52.5	Silicon	Si IV	28
Cobalt	Co II VI	59	Silver	Ag I	108
Copper	Cu II	63.5	Sodium	Na I	23
Didymium	Di IV	144	Strontium	Sr II	87.5
Erbium	Er III	170.6	Sulphur	S II IV VI	32
Fluorine	F I	19	Tantalium	Ta V	182
Gallium	Ga II IV	69.9	Tellurium	Te II IV VI	125
Germanium	Ge IV	73.3	Thallium	Tl I III	204
Gold	Au III	197	Thorium	Th IV	231.5
Hydrogen	H I	1	Tin	Sn IV	118
Indium	In III	113	Titanium	Ti IV	48
Iodine	I I VII	127	Tungsten (Wolfra-		
Iridium	Ir IV VI	193	mium)	W IV	184
Iron	Fe II III VI	56	Uranium	Ur VI	240
Lanthanum	La IV	139	Vanadium	V V	51
Lead	Pb II IV	207	Wolframium (Tung-		
Lithium	Li I	7	sten)	W VI	184
Magnesium	Mg II	24	Ytterbium	Yb IV	172.6
Manganese	Mn II VII	55	Yttrium	Y III	88
Mercury	Hg II	200	Zinc	Zn II	65
Molybdenum	Mo VI	96	Zirconium	Zr IV	90
Nickel	Ni II	59			

Specific Gravity of Acetic Acid Solutions at 15° C.
(Oudemans.)

Specific Gravity	% $C_2H_4O_2$	Specific Gravity	% $C_2H_4O_2$	Specific Gravity	% $C_2H_4O_2$
0.9992	0	1.0459	34	1.0725	68
1.0007	1	1.0470	35	1.0729	69
1.0022	2	1.0481	36	1.0733	70
1.0037	3	1.0492	37	1.0737	71
1.0052	4	1.0502	38	1.0740	72
1.0067	5	1.0513	39	1.0742	73
1.0083	6	1.0523	40	1.0744	74
1.0098	7	1.0533	41	1.0746	75
1.0113	8	1.0543	42	1.0747	76
1.0127	9	1.0552	43	1.0748	77
1.0142	10	1.0562	44	1.0748	78
1.0157	11	1.0571	45	1.0748	79
1.0171	12	1.0580	46	1.0748	80
1.0185	13	1.0589	47	1.0747	81
1.0200	14	1.0598	48	1.0746	82
1.0214	15	1.0607	49	1.0744	83
1.0228	16	1.0615	50	1.0742	84
1.0242	17	1.0623	51	1.0739	85
1.0256	18	1.0631	52	1.0736	86
1.0270	19	1.0638	53	1.0731	87
1.0284	20	1.0646	54	1.0726	88
1.0298	21	1.0653	55	1.0720	89
1.0311	22	1.0660	56	1.0713	90
1.0324	23	1.0666	57	1.0705	91
1.0337	24	1.0673	58	1.0696	92
1.0350	25	1.0679	59	1.0686	93
1.0363	26	1.0685	60	1.0674	94
1.0375	27	1.0691	61	1.0660	95
1.0388	28	1.0697	62	1.0644	96
1.0400	29	1.0702	63	1.0625	97
1.0412	30	1.0707	64	1.0604	98
1.0424	31	1.0712	65	1.0580	99
1.0436	32	1.0717	66	1.0553	100
1.0447	33	1.0721	67		

Liquor Ammoniae.

TABLE ACCORDING TO LUNGE AND WIERNIK.*

Specific Gravity at 15° C.	% NH_3	Grams per Liter NH_3	Specific Gravity at 15° C.	% NH_3	Grams per Liter NH_3
1.000	0.00	0.0	0.940	15.63	146.9
0.998	0.45	4.5	0.938	16.22	152.1
0.996	0.91	9.1	0.936	16.82	157.4
0.994	1.37	13.6	0.934	17.42	162.7
0.992	1.84	18.2	0.932	18.03	168.1
0.990	2.31	22.9	0.930	18.64	173.4
0.988	2.80	27.7	0.928	19.25	178.6
0.986	3.30	32.5	0.926	19.87	184.2
0.984	3.80	37.4	0.924	20.49	189.3
0.982	4.30	42.2	0.922	21.12	194.7
0.980	4.80	47.0	0.920	21.75	200.1
0.978	5.30	51.8	0.918	22.39	205.6
0.976	5.80	56.6	0.916	23.03	210.9
0.974	6.30	61.4	0.914	23.68	216.3
0.972	6.80	66.1	0.912	24.33	221.9
0.970	7.31	70.9	0.910	24.99	227.4
0.968	7.82	75.7	0.908	25.65	232.9
0.966	8.33	80.5	0.906	26.31	238.3
0.964	8.84	85.2	0.904	26.98	243.9
0.962	9.35	89.9	0.902	27.65	249.4
0.960	9.91	95.1	0.900	28.33	255.0
0.958	10.47	100.3	0.898	29.01	260.5
0.956	11.03	105.4	0.896	29.69	266.0
0.954	11.60	110.7	0.894	30.37	271.5
0.952	12.17	115.9	0.892	31.05	277.0
0.950	12.74	121.0	0.890	31.75	282.6
0.948	13.31	126.2	0.888	32.50	288.6
0.946	13.88	131.3	0.886	33.25	294.6
0.944	14.46	136.5	0.884	34.10	301.4
0.942	15.04	141.7	0.882	34.95	308.3

* Zeit. f. angew. Chem. **1889**, 183.

Hydrochloric Acid.

TABLE ACCORDING TO LUNGE AND MARCHLEWSKI.*

Degrees Twaddell	Specific Gravity at 15° C.	100 Grams of Solution correspond to Grams of HCl	1 Liter contains Grams of HCl	Degrees Twaddell	Specific Gravity at 15° C.	100 Grams of Solution correspond to Grams of HCl	1 Liter contains Grams of HCl
0	1.000	0.16	1.6	21	1.105	20.97	232
1	1.005	1.15	12	22	1.110	21.92	243
2	1.010	2.14	22	23	1.115	22.86	255
3	1.015	3.12	32	24	1.120	23.82	267
4	1.020	4.13	42	25	1.125	24.78	278
5	1.025	5.15	53	26	1.130	25.75	291
6	1.030	6.15	64	27	1.135	26.70	303
7	1.035	7.15	74	28	1.140	27.66	315
8	1.040	8.16	85	29	1.145	28.61	328
9	1.045	9.16	96	30	1.150	29.57	340
10	1.050	10.17	107	31	1.155	30.55	353
11	1.055	11.18	118	32	1.160	31.52	366
12	1.060	12.19	129	33	1.165	32.49	379
13	1.065	13.19	141	34	1.170	33.46	392
14	1.070	14.17	152	35	1.175	34.42	404
15	1.075	15.16	163	36	1.180	35.39	418
16	1.080	16.15	174	37	1.185	36.31	430
17	1.085	17.13	186	38	1.190	37.23	443
18	1.090	18.11	197	39	1.195	38.16	456
19	1.095	19.06	209	40	1.200	39.11	469
20	1.100	20.01	220				

* Zeit. f. angew. Chem. **1891**, 133.

Nitric Acid.

TABLE ACCORDING TO LUNGE AND REY.*

Degrees Twaddell	Per cent by Weight of HNO_3	Grams per Liter of HNO_3	Degrees Twaddell	Per cent by Weight of HNO_3	Grams per Liter of HNO_3	Degrees Twaddell	Per cent by Weight of HNO_3	Grams per Liter of HNO_3
0	0.10	1	35	28.63	336	70	55.79	753
1	1.00	10	36	29.38	347	71	56.66	768
2	1.90	19	37	30.13	357	72	57.57	783
3	2.80	28	38	30.88	367	73	58.48	798
4	3.70	38	39	31.62	378	74	59.39	814
5	4.60	47	40	32.36	388	75	60.30	829
6	5.50	57	41	33.09	399	76	61.27	846
7	6.38	66	42	33.82	409	77	62.24	862
8	7.26	75	43	34.55	420	78	63.23	879
9	8.13	85	44	35.28	430	79	64.25	896
10	8.99	94	45	36.03	441	80	65.30	914
11	9.84	104	46	36.78	452	81	66.40	933
12	10.68	113	47	37.53	463	82	67.50	952
13	11.51	123	48	38.29	475	83	68.63	971
14	12.33	132	49	39.05	486	84	69.80	991
15	13.15	141	50	39.82	498	85	70.98	1011
16	13.95	151	51	40.58	509	86	72.17	1032
17	14.74	160	52	41.34	521	87	73.39	1053
18	15.53	169	53	42.10	533	88	74.68	1075
19	16.32	179	54	42.87	544	89	75.98	1098
20	17.11	188	55	43.64	556	90	77.28	1121
21	17.89	198	56	44.41	568	91	78.60	1144
22	18.67	207	57	45.18	581	92	79.98	1168
23	19.45	217	58	45.95	593	93	81.42	1193
24	20.23	227	59	46.72	605	94	82.90	1219
25	21.00	236	60	47.49	617	95	84.45	1246
26	21.77	246	61	48.26	630	96	86.05	1274
27	22.54	256	62	49.07	643	97	87.70	1302
28	23.31	266	63	49.89	656	98	89.60	1335
29	24.08	276	64	50.71	669	99	91.60	1369
30	24.84	286	65	51.53	683	100	94.09	1411
31	25.60	296	66	52.37	697	101	96.39	1451
32	26.36	306	67	53.22	710	102	98.10	1481
33	27.12	316	68	54.07	725	103	99.07	1501
34	27.88	326	69	54.93	739	104	99.67	1515

* Zeit. f. angew. Chem. **1891**, 165.

Sulphuric Acid.

TABLE ACCORDING TO LUNGE AND ISLER.*

Degrees Twaddell at 15° C.	Grams of H_2SO_4 per 100 Grams	Kilo H_2SO_4 per Liter	Degrees Twaddell at 15° C.	Grams of H_2SO_4 per 100 Grams	Kilo H_2SO_4 per Liter	Degrees Twaddell at 15° C.	Grams of H_2SO_4 per 100 Grams	Kilo H_2SO_4 per Liter	Degrees Twaddell at 15° C.	Grams of H_2SO_4 per 100 Grams	Kilo H_2SO_4 per Liter
40	27.32	0.328	73	46.41	0.633	106	62.53	0.957	139	76.73	1.301
41	27.95	0.337	74	46.94	0.643	107	63.00	0.967	140	77.17	1.312
42	28.58	0.346	75	47.47	0.653	108	63.43	0.977	141	77.60	1.323
43	29.21	0.355	76	48.00	0.662	109	63.85	0.987	142	78.04	1.334
44	29.84	0.364	77	48.53	0.672	110	64.26	0.996	143	78.48	1.346
45	30.48	0.373	78	49.06	0.682	111	64.67	1.006	144	78.92	1.357
46	31.11	0.382	79	49.59	0.692	112	65.08	1.015	145	79.36	1.369
47	31.70	0.391	80	50.11	0.702	113	65.49	1.025	146	79.80	1.381
48	32.28	0.400	81	50.63	0.711	114	65.90	1.035	147	80.24	1.392
49	32.86	0.409	82	51.15	0.721	115	66.30	1.044	148	80.68	1.404
50	33.43	0.418	83	51.66	0.730	116	66.71	1.054	149	81.12	1.416
51	34.00	0.426	84	52.15	0.740	117	67.13	1.064	150	81.56	1.427
52	34.57	0.435	85	52.63	0.750	118	67.59	1.075	151	82.00	1.439
53	35.14	0.444	86	53.11	0.759	119	68.05	1.085	152	82.44	1.451
54	35.71	0.454	87	53.59	0.769	120	68.51	1.096	153	82.88	1.463
55	36.29	0.462	88	54.07	0.779	121	68.97	1.107	154	83.32	1.475
56	36.87	0.472	89	54.55	0.789	122	69.43	1.118	155	83.90	1.489
57	37.45	0.481	90	55.03	0.798	123	69.89	1.128	156	84.50	1.504
58	38.03	0.490	91	55.50	0.808	124	70.32	1.139	157	85.10	1.519
59	38.61	0.500	92	55.97	0.817	125	70.74	1.150	158	85.70	1.534
60	39.19	0.510	93	56.43	0.827	126	71.16	1.160	159	86.30	1.549
61	39.77	0.519	94	56.90	0.837	127	71.57	1.170	160	86.90	1.564
62	40.35	0.529	95	57.37	0.846	128	71.99	1.181	161	87.60	1.581
63	40.93	0.538	96	57.83	0.856	129	72.40	1.192	162	88.30	1.598
64	41.50	0.548	97	58.28	0.866	130	72.87	1.202	163	89.05	1.621
65	42.08	0.557	98	58.74	0.876	131	73.23	1.212	164	90.05	1.639
66	42.66	0.567	99	59.22	0.886	132	73.64	1.222	165	91.00	1.661
67	43.20	0.577	100	59.70	0.896	133	74.07	1.233	166	92.10	1.685
68	43.74	0.586	101	60.18	0.906	134	74.51	1.244	167	93.43	1.713
69	44.28	0.596	102	60.65	0.916	135	74.97	1.256	168	95.60	1.759
70	44.82	0.605	103	61.12	0.926	136	75.42	1.267			
71	45.35	0.614	104	61.59	0.936	137	75.86	1.278			
72	45.88	0.624	105	62.06	0.946	138	76.30	1.289			

* Zeit. f. angew. Chem. **9**, 129.

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